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THE INFRA-RED ABSORPTION BANDS OF METHANE

By J. P. COOLEY

ABSTRACT

Previous investigations on methane have shown three absorption regions which Coblentz places at 7.7 μ, 3.31 μ, and 2.35 μ. By using the higher resolving-power of a grating spectrometer all of these have been partially resolved into lines. About fifty lines in the region of 3.31 μ were measured and arranged in positive and negative series. Between these, and masking part of the negative or longer wave-length series, lies a narrow region of intense absorption corresponding to the zero branch. Here the lines are too closely packed to be resolved but the complex structure is indicated by a large shift of the maximum absorption when the thickness of the layer of gas is changed. The band at 7.7 μ is similar to the one at 3.31 μ. Twelve lines in the negative series and eighteen in the positive series have been measured but again in the zero branch no fine structure appears. The resolving-power of the apparatus was insufficient to show much detail in the band at 2.35 μ. In the positive and negative branches near 7.7 μ the frequency difference between adjacent lines is 9.77 cm^{-1} and near 3.31 μ it is 5.41 $cm.^{-1}$ A faint band of twelve lines near 3.5 μ has a frequency difference approximating 15.3 $cm.^{-1}$

INTRODUCTION

John Tyndall,[1] in a characteristically interesting memoir published in 1862, presented the results of his researches on the absorption of undispersed radiation by gases. He showed that air, oxygen, nitrogen, and hydrogen are nearly transparent, whereas carbon monoxide, hydrogen chloride, methane, and other gases with more complicated molecules are fairly opaque. Many years later during a survey of the infra-red region with a prism spectrometer Angstrom[2] found absorption bands for methane near 2.12 μ, 3.18 μ, and 10.59 μ.

[1] *Philosophical Transactions*, **152**, 59, 1862.

[2] *Öfversigt af Kongl. Vetenskaps-Akad. Förh.*, **47**, 331, 1890.

He concluded that the wave-length of maximum absorption shifts with the thickness of the absorbing layer of gas and that apparently Lambert's law does not hold. Coblentz,[1] however, pointed out that the wave-lengths greater than 5 μ published by Angstrom are very inaccurate, and he located simple absorption maxima for methane at 2.35 μ, 3.31 μ, and 7.7 μ.

Rubens and von Wartenberg[2] have explored certain absorption spectra in the far infra-red by the method of *Reststrahlen*. They give the following results for a column of methane 40 cm in length:

Wave-Length	Transmission Percentage
23 μ	91.0
52	94.3
110	99.2
314	100.0

Recent advances in infra-red spectroscopy have made possible a detailed study of the bands located by these observers. In but few gases, notably *HF*, *HCl*, *HBr*, H_2O, CO_2, and *CO*, is the fine structure of the bands in this region known, and with some of these substances the complete data is still lacking. That such measurements are important is indicated by the great amount of theory that has been built on this rather meager foundation. Methane (CH_4) played an important rôle in the early history of stereochemistry, and the behavior of this gas led chemists to believe that, in the molecule, the four hydrogen nuclei occupy the corners of a regular tetrahedron with the carbon atom at the center. From the symmetry of such a model, simple band structure is to be anticipated; from a small moment of inertia about an axis through the center of gravity, widely spaced lines. Accordingly, the infra-red absorption bands of gaseous methane were chosen for the subject of the present investigation.

APPARATUS

For the earlier part of the work a spectrometer designed by W. W. Sleator,[3] and used by him in the study of the bands of water-vapor, was available. In this instrument the radiation first passes

[1] "Investigations of Infra-Red Spectra," *Publications of the Carnegie Institution of Washington, D.C.*, p. 39, 1905.

[2] *Verh. d. D. Phys. Gesell.*, **13**, 796, 1911.

[3] *Astrophysical Journal*, **48**, 125, 1918.

through a large rock-salt prism in such a way that only a selected range of wave-lengths is allowed to enter the slit of the grating spectrometer. Thus, overlapping of the spectral orders can be entirely avoided. The source of light was a Nernst glower supplied with power from the university mains. Since the lamp was used during hours when the load on these lines is very small, the voltage fluctuated but little.

The thermopile, constructed by Coblentz, is the one used in previous work with this spectrometer, but the Paschen astatic needle galvanometer, built by Sleator and formerly employed to measure the feeble currents from the thermopile, has been replaced by another of the same type constructed in this laboratory. With the illuminated scale at a distance of 2 m the figure of merit is $84.7\times10^{-10}T^{-1.88}$ amperes per millimeter, where T is the time required for the instrument to deflect and return to its original position. For the undamped motion of the suspension, the figure of merit depends upon the inverse square of the period, but with light systems in air the sensitivity varies less rapidly with period. The instrument was always overdamped. Generally, the galvanometer was adjusted to a period of six or seven seconds, corresponding to a figure of merit of 2.5×10^{-10} amperes per millimeter. The resistance, about 2.2 ohms, nearly equals that of the thermopile. Unfortunately, this instrument was not protected from vibrations of the building nor was it shielded magnetically, consequently all readings were taken during the quiet hours between one and five o'clock in the morning.

The grating is an admirable echelette ruled in this laboratory by Dr. Barker. The form of the grooves is such that a large proportion of the energy of the spectral region between 6μ and 8μ is thrown into the first diffracted image. The spacing, 2800 lines per inch, gives good dispersion in this region but, of course, is not so satisfactory for shorter wave-lengths. The ruled area measures 10×16 cm, and covers all but a narrow margin of the polished surface.

Another spectrometer designed by E. F. Barker[1] served for work at shorter wave-lengths. Except for a slight change in the use of the prism, the arrangement is similar to the one just described. The thermopile, however, has a considerably higher resistance (14.5

[1] *Astrophysical Journal*, **55**, 391, 1922.

ohms), and is connected to a Leeds and Northrup high-sensitivity galvanometer of the D'Arsonval type. This detecting system proved to be very satisfactory. Although not so sensitive as the apparatus previously used, it is much more stable. When the scale is at a distance of 1 m from the mirror, the galvanometer has a figure of merit of 2.4×10^{-9} amperes per millimeter, but was considerably overdamped, twenty seconds being required for a single deflection. When the size of the deflections permitted, a critical damping resistance of 19 ohms was added to the 26.5 ohms already in the circuit. The advantage of a quick and definite throw more than offset the decrease in deflection.

Again, one of Dr. Barker's echelettes ruled with 7200 lines to the inch proved most valuable, particularly in the region from 2μ to 4μ. The effective surface is 13 cm long by 8 cm high. The glower, supplied from the Detroit Edison Company's 220-volt mains and ballasted with a large resistance, was fairly steady even during hours when other loads were on the line.

Not fewer than twelve cells ranging in length from $\frac{1}{2}$ mm to 30 cm were used as containers for the absorbing gas at various times in the progress of the investigations. Nearly all of the cells were hollow brass cylinders with thin sheets of mica for ends. Soft wax cements the mica to the brass and prevents the leakage of gas. These mica windows had a thickness of about 0.04 mm and were sufficiently transparent, except between 8μ and 9μ. For this region polished plates of rock salt replaced the mica

METHODS AND RESULTS

Methane was generated by heating together in an iron crucible a mixture of two parts by weight of soda lime (CaO, 67 per cent, and Na_2O, 33 per cent) and one part of fused anhydrous sodium acetate. Since the chemicals contained only very small traces of impurities (about 0.01 per cent), no further attempt was made to purify them. The gas generated in this way bubbled through two washing towers of sodium hydroxide solution and five towers of concentrated sulphuric acid. Thus the methane was freed from impurities, principally water-vapor and ethylene, which may be present. The cells were filled by downward displacement of air and, after a volume of gas several

times as large as the capacity of the absorption chamber had passed through, the openings were tightly closed. The cells containing methane generally occupied a position just in front of the first slit of the prism spectrometer. Since the mica windows of the cell absorb some of the radiation, it is necessary to introduce compensating windows into the beam when the cell is removed. The most satisfactory results were obtained when the compensating windows and the windows of the cell were cut from the same sheet of mica.

In the actual measurements the grating and prism were turned to positions appropriate to the wave-length under investigation, and the galvanometer deflections produced by opening the shutter were read both when the cell was in the beam and when it was replaced by the compensating windows. For each position of the grating, from eight to sixteen such readings were taken. These data properly reduced give the fraction of the incident energy absorbed by the gas. The same procedure repeated at intervals approximating 0.001 μ furnished curves such as those shown in Figures 1, 2, and 3.

Thus, the single maximum of absorption observed by Coblentz at 7.7 μ resolves into thirty or more lines with a very intense region of absorption at the center. Figure 2 presents, in part, the analysis of the band near 3.31 μ. Here about sixty lines have been measured. Figure 3 indicates that the region of 2.35 μ is more complicated than the other bands and that evidently the resolving-power is insufficient to reveal the fine structure.

With the 2800-line grating visual methods of calibration fail and the mercury line at 1.0140 μ does not possess measurable intensity. Several calibrations were made, however, by means of the lines $+6$ to -6 in the band of hydrogen chloride at 3.46 μ, for which accurate wave-lengths have been published by W. F. Colby and C. F. Meyer.[1] Thus in the equation

$$n\lambda = K \sin(\theta - \theta_0)$$

log K is $1.24516 + 0.000011\,(t-20)$ where t is the temperature of the grating. The position of the central image was determined at the beginning and again at the end of each day's work. The 7200-line grating gave sufficient energy so that even with the D'Arsonval

[1] *Astrophysical Journal*, **53**, 300, 1921.

galvanometer measurements were possible on the first-, second-, and third-order spectra of the mercury line mentioned above. Sixteen calibrations yielded a mean value of 0.847208+0.0000074 (t−20)

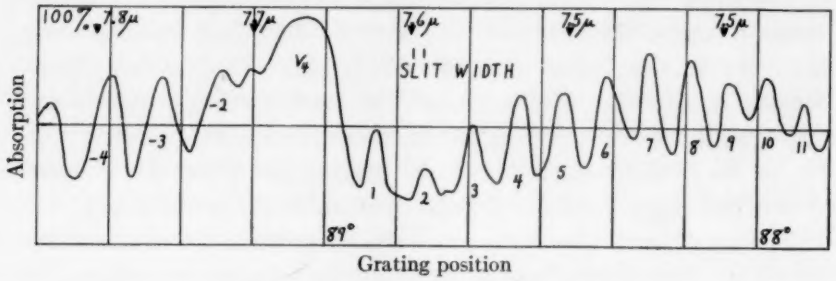

FIG. 1.—A portion of the band at 7.7 μ

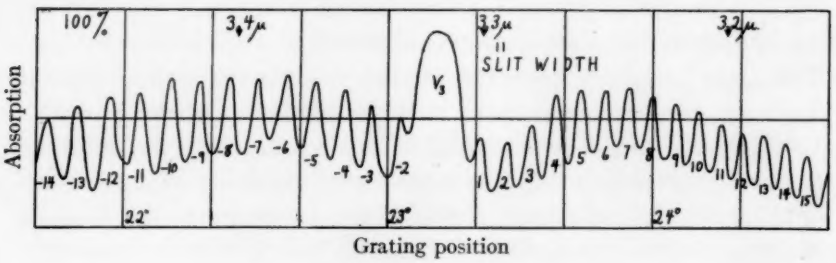

FIG. 2.—Portion of the band at 3.31 μ

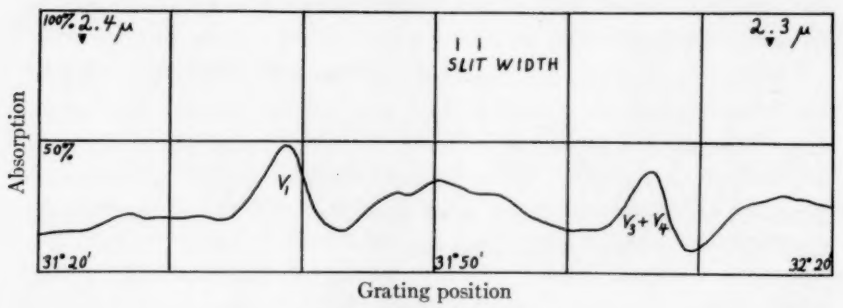

FIG. 3.—Band at 2.35 μ

for log K, in good agreement with 0.847207 arrived at several months before by Dr. Barker from measurements on the bands of hydrogen chloride. The temperature corrections were computed from coefficients of expansion for the material on which the gratings were ruled.

The slits of the spectrometers were usually adjusted to a width

of $\frac{1}{2}$ mm. A short calculation shows that with the 2800-line grating the slit of the thermopile includes ranges of 86, 84, and 70 A, respectively, in the first-order spectra at 2.35 μ, 3.31 μ, and 7.7 μ. With the 7200-line grating the thermopile slit includes 27 A at 3.31 μ and 31 A at 2.35 μ.

TABLE I

REGION OF 7.7 μ MEASURED WITH 2800-LINE GRATING

m	Intensity (5.0-cm Cell)	Wave-Length	Frequency
−12	5	8.0802 μ	1237.6 cm^{-1}
11	5	8.0469	1242.7
10	6	8.0111	1248.3
9	5	7.9708	1254.6
8	6	7.9296	1261.1
7	5	7.8974	1266.2
6	5	7.8677	1271.0
5	6	7.8287	1277.4
4	7	7.7913	1283.5
3	7	7.7569	1289.2
− 2	7	7.7140	1296.3
(App. V_4)	10	7.6672	1304.3
1	5	7.6203	1312.3
2	3	7.5929	1317.0
3	5	7.5583	1323.0
4	6	7.5283	1328.3
5	6	7.5000	1333.3
6	7	7.4722	1338.3
7	8	7.4463	1342.9
8	8	7.4193	1347.8
9	7	7.3936	1352.5
10	7	7.3708	1356.7
11	6	7.3463	1361.2
12	5	7.3234	1365.5
13	5	7.3017	1369.5
14	4	7.2761	1374.4
15	3	7.2557	1378.2
16	2	7.2289	1383.3
17	2	7.2071	1387.5
18	2	7.1806	1392.6
19	2	7.1615	1396.4
20	2	7.1381	1400.9
21	1	7.1151	1405.5

Table I gives the wave-lengths, frequencies, and intensities for the lines in the band at 7.7 μ as measured with the 2800-line grating. By careful work on the quietest nights observations were made on the spectrum as far as 8.5 μ. When the ordinal numbers of the lines are chosen as shown in the table the frequencies may be represented by

$$\nu = 1320.4 + 5.409\, m - 0.0377\, m^2 .$$

TABLE II

REGION OF 3.31 μ MEASURED WITH 7200-LINE GRATING

Designation	Intensity (6.6-cm Cell)	Wave-Length	Frequency
(App. 2 V_4)	2	3.8466 μ	2599.7 cm^{-1}
−XI	1	3.7636	2657.0
X	1	3.7450	2670.2
IX	1	3.7269	2683.2
VIII	1	3.7075	2697.2
VII	2	3.6873	2712.0
VI	2	3.6667	2727.2
V	3	3.6462	2742.6
−26	1	3.6358	2750.4
IV	2	3.6257	2758.1
III	2	3.6063	2772.9
II	3?	3.5847	2789.6
−22?	3?	3.5807	2792.7
.....	2	3.5710	2800.3
−I	3?	3.5643	2805.6
(App. V_2+V_4)	3	3.5409	2824.1
I?	2?	3.5254	2836.6
−17?	1?	3.5168	2843.5
16	3	3.5027	2854.9
15	4	3.4896	2865.7
14	5	3.4771	2876.0
13	6	3.4648	2886.2
12	6	3.4520	2896.9
11	6	3.4397	2907.2
10	7	3.4271	2917.9
9	7	3.4153	2928.0
8	7	3.4035	2938.2
7	7	3.3915	2948.5
6	7	3.3799	2958.7
5	7	3.3682	2968.9
4	6	3.3566	2979.2
3	6	3.3453	2989.3
−2	5	3.3336	2999.8
(App. V_3)	9	3.3185	3013.4
1	4	3.3012	3029.2
2	4	3.2905	3039.1
3	5	3.2800	3048.8
4	6	3.2700	3058.1
5	6	3.2598	3067.7
6	6	3.2499	3077.0
7	7	3.2400	3086.4
8	6	3.2306	3095.4
9	6	3.2208	3104.8
10	6	3.2115	3113.8
11	5	3.2023	3122.8
12	5	3.1932	3131.7
13	4	3.1843	3140.4
14	4	3.1755	3149.1
15	3	3.1667	3157.9
16	3	3.1580	3166.6
17	2	3.1493	3175.3
18	2	3.1416	3183.1
19	1	3.1328	3192.0
20	1	3.1257	3199.3
21	0	3.1168	3208.4
22	0	3.1096	3215.8
23	0	3.0991	3226.7
24	0	3.0909	3235.3

Three complete sets of readings were made with the 2800-line grating on the band at 3.31 μ and three more with the 7200-line grating. Table II summarizes the results. Again the method of least squares was employed to fit the data to the parabolic formula

$$\nu = 3019.3 + 9.771\, m - 0.0351\, m^2 .$$

Neither the 2800- nor the 7200-line grating revealed any definite fine structure in the region of 2.35 μ, but Table III contains the wave-lengths of the few measurable absorption maxima.

TABLE III

REGION OF 2.35 μ MEASURED WITH 7200-LINE GRATING

Designation	Intensity (6.6-cm Cell)	Wave-Length	Frequency
(App. V_2+2V_4)	1	2.4262 μ	4121.7 cm^{-1}
(App. V_1)	5	2.3714	4216.9
(App. V_3+V_4)	4	2.3178	4314.4
(App. V_2+V_3)	1	2.2008	4543.8

CONCLUSIONS

While the general question of interpretation is left to Dr. Dennison, whose paper follows, it will not be amiss to point out certain peculiarities of structure which distinguish this band system from those previously observed. The regions of intense absorption near the centers of the bands mapped in Figures 1 and 2 are evidently unresolved zero branches, similar to those observed in the photographic regions of the spectrum; while the positive and negative branches are seen on either side of the center. Other experimenters, notably Burmeister,[1] have found bands of this general description, but under the lower resolving-powers used by them the true character of the absorption was not so apparent. Computation indicates that the spacing between the lines of the zero branch is far too small to be detected by the apparatus. It was shown in another way, however, that this maximum is not a simple line but a band. If a series of lines such as the positive branch in Figure 2 is mapped for various increasing thicknesses of absorbing gas it is found that the center of gravity of the system as a whole shifts toward higher values of $|m|$. This is the effect observed by Angstrom in unresolved bands. The explanation is simple. For a moderate length of absorbing gas the most intense

[1] *Verh. d. D. Phys. Gesell.*, **15**, 589, 1913.

lines for methane at room temperature are near $|m|=6$. If the absorption cell is exchanged for a much longer one, the percentage of absorption at the strongest lines, being already so great, cannot increase much; whereas the lines of higher number become many times more intense. Hence the center of gravity of the band shifts toward lines of higher ordinal number. This effect for the zero branch at 3.31 μ is shown in Figure 4. It appears, also, that the zero line of this series falls on the zero line of the positive and negative branches.

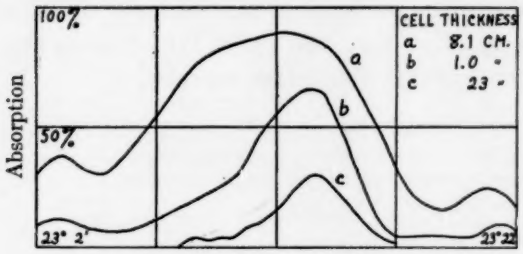

FIG. 4.—Showing shift of the zero branch at 3.31 μ

The frequency difference between adjacent lines near 3.31 μ is 9.77 cm^{-1} and near 7.7 μ it is 5.41 $cm.^{-1}$ Furthermore a rather faint series, designated in Table II by Roman numerals, has been found near 3.5 μ. This band has the peculiarity, here observed for the first time in the infra-red region, of converging to a head on the side of the band toward longer wave-lengths. The frequency differences for these lines are about 15.3 cm^{-1}, which is nearly the sum of the frequency differences mentioned above. On the basis of the quantum theory the moment of inertia of the molecule is given approximately[1] by

$$I=\frac{h}{4\pi^2(\Delta\nu)}$$

where h is Planck's constant and $\Delta\nu$ the frequency difference between adjacent lines in the band spectrum. The foregoing frequency differences for the three sets of bands give for the moments of inertia of the molecule of methane 5.66×10^{-40}, 10.2×10^{-40}, and 3.61×10^{-40} gm cm^2, respectively. Furthermore, the formula

$$I=\frac{\frac{3}{2}RT}{4\pi^2N\bar{\nu}_r^2}$$

given by Eucken,[2] in which $R/N=1.372\times10^{-16}$ ergs per degree, T the absolute temperature, and $\bar{\nu}_r$ the most probable rotational frequency

[1] A. Kratzer, *Annalen der Physik*, **67**, 127, 1922.

[2] *Zeits. Elektrochem.*, **26**, 377, 1920.

of the methane molecule, affords a rough check on these numbers. $\bar{\nu}_r$ is here interpreted as one-half of the frequency difference between the most intense line of the positive branch and the corresponding line of the negative branch. This quantity cannot easily be determined from grating spectra, but the best values available yield 4.3×10^{-40} and 11×10^{-40} gm cm^2, corresponding to the first two values above.

Guye and Rüdy[1] recently calculated the diameter of the molecule of methane from electrical measurements. Their result is somewhat larger than those deduced from the foregoing moments of inertia, but due to the uncertainty in the meaning of the term "diameter" no exact check is to be expected. Measurements of viscosity furnish a molecular diameter slightly less than that given by Guye and Rüdy.

Much remains to be done in mapping the absorption spectrum of methane, and with the help of more efficient apparatus now in process of construction the author hopes soon to carry the task more nearly to completion.

Methane was not the only substance investigated. Diligent search for the "first harmonic" of hydrogen fluoride revealed no measurable absorption even with cells 1 m in length. Next, the spectrum of hydrogen iodide was explored in the region between 2 μ and 6 μ with no better success. Since then, Schäfer and Thomas[2] announced the discovery of a rather faint unresolved band for hydrogen fluoride near 1.25 μ, the position predicted by Imes. The same investigators were unable to find any trace of infra-red absorption for hydrogen iodide.

In conclusion, the writer wishes to express his indebtedness to Professor Randall, under whose direction the work here presented was done. Dr. Sleator and Dr. Barker gave valuable suggestions on experimental technique and also on the interpretation of the results. During his visit to the university in 1922 Professor Arnold Sommerfeld examined the data then available and discussed the meaning of the bands from the standpoint of quantum mechanics.

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[1] *Comptes Rendus*, **174**, 382, 1922.

[2] *Zeitschrift für Physik*, **12**, 330, 1923.

THE MOLECULAR STRUCTURE AND INFRA-RED SPECTRUM OF METHANE

By DAVID M. DENNISON

ABSTRACT

An attempt is made to treat the molecule of methane from the standpoint of the quantum theory and to determine the frequencies of radiation which it may absorb or emit. The assumption is made that in the normal state the four hydrogen nuclei lie at the corners of a regular tetrahedron while the carbon nucleus lies at the center. It is further assumed that following an infinitesimal displacement of the nuclei the potential energy depends upon the squares of the displacements along the lines between the nuclei. The model yields four normal frequencies, ν_1, ν_2, ν_3, and ν_4, which through the use of two undetermined constants may be made to coincide quite closely with the four fundamental frequencies found experimentally by J. P. Cooley. By studying the change of the electric moment it is possible to predict the relative intensities of these four fundamental bands. The agreement between the theoretical and experimental intensities is quite satisfactory. Dr. Cooley has found that the spacing of the fine structure lines of the band to be correlated with the frequency ν_4 is approximately half the corresponding spacing between the lines of the ν_3 band. In the present paper it is shown that such a phenomenon seems capable of being explained under the assumption that the molecule of methane possesses a resultant electronic angular momentum fixed in direction in the molecule of amount $\frac{1}{2}\left(\frac{h}{2\pi}\right)$.

I. INTRODUCTION

In the preceding paper Dr. J. P. Cooley has given the results of an experimental investigation of the infra-red spectrum of methane. He has determined with great accuracy the centers of a considerable number of bands, and has resolved two of the bands into a series of regularly spaced sharp lines. It is obvious that there must exist a very intimate connection between the mechanical structure and properties of a molecule and the frequencies of radiation which it may absorb. In the present paper an attempt is made to find this connection for the case of methane, and both to interpret the absorption spectrum and to study the mechanics of the molecule.

Before considering in detail the spectrum of methane it may be well to review briefly those characteristics of the vibration spectrum of any general molecule on which the work is based. It is well known that the frequency of such nuclear vibrations is very slow in comparison with the orbital frequencies of the electrons, and hence only the average effect of the electrons on the nuclei need be considered. In the first vibrational states of a molecule the amplitude of vibra-

tion is usually small and in first approximation may be considered to be infinitesimal. Employing this assumption, the potential and kinetic energies of a molecular system of s degrees of freedom are known to be positive, definite, quadratic forms in the s displacement co-ordinates, defining the system, and their time derivatives, respectively. The motion of such a system may be resolved in terms of the so-called normal modes of vibration. The characteristics of these normal vibrations are that the energy of each mode is independent and that the corresponding normal co-ordinate obeys the conditions for simple harmonic motion. The transformation to normal co-ordinates forms the natural means of treating the problem by the method of separation of variables, and it is clear that each of the normal vibrations should be quantized independently. Thus this system in a radiation field will behave as a series of independent Planck oscillators whose characteristic frequencies are identical with the frequencies of the normal modes of vibration. The intensity with which any one of these oscillators absorbs or emits radiation will depend upon the amplitude of the motion of the electric moment for the normal mode under consideration. Very often a number n of the normal frequencies coincide, and in this case the corresponding Planck oscillator is one of n dimensions. The behavior of such an oscillator in a radiation field is entirely similar to the behavior of a simple Planck oscillator, with the one exception that the charged particles move along paths which may be arbitrarily oriented in n dimensions.

As is well known, the application of the correspondence principle to such a simplified system composed of a number of independent oscillators leads to the conclusion that no harmonic or combination frequencies may be absorbed or emitted. The nuclei of the real molecule vibrate with finite amplitudes, and it is to be expected that the results of the analysis of the foregoing simplified system will only approximately agree with the observed data. Thus in the observed infra-red spectra it is found that harmonic and combination frequencies do actually appear although usually with very slight intensity. The faintness of these bands may often be taken as an indication of the magnitude of the errors involved in considering the motion to be infinitesimal.

2. THE NORMAL MODES OF VIBRATION OF A SIMPLIFIED MODEL OF METHANE

The observed properties of methane show that the molecule must possess a highly symmetrical structure. Chemically, the four hydrogen atoms are equivalent since only one compound may be formed regardless of which one of the hydrogen atoms is replaced by another atom or group of atoms. It is known, moreover, that these four equivalent hydrogen atoms do not lie in a plane, for, if three of them are replaced by three dissimilar atoms as *Cl*, *Br*, and *F*, two distinct compounds may be formed which have identical properties with the exception that they polarize light in opposite senses. It seems clear that the one compound might be considered as the mirrored image of the other. Measurements of the dielectric constant of methane show that the average electric moment of the normal molecule must be very small, probably zero, attesting further to the symmetry of the structure.

The evidence just mentioned, as well as the evidence from other sources, seems to show that in the normal state the four hydrogen particles lie at the corners of a regular tetrahedron while the carbon particle lies at the center of the tetrahedron. In the following work a model of this sort will be considered, and the attempt will be made to study its motion and to correlate it with the observed spectrum of methane. In accordance with the general treatment of the problem of molecular vibration outlined in the introduction, the assumption will be made that the amplitude of vibration may be considered to be infinitesimal. The kinetic energy may be expressed as a positive definite quadratic form whose coefficients depend upon the geometric form of the model and upon the masses of the particles, while the coefficients of the corresponding form for the potential energy depend upon the nature of the forces brought into play by an arbitrary displacement of the nuclei. A study of these forces may best be made by considering the general characteristics of the average electronic distribution.

The electrostatic field due to the five nuclei has a predominant spherical symmetry about the carbon nucleus, but superimposed upon this symmetrical field there exist weaker electrostatic fields which possess spherical symmetry about each of the hydrogen nuclei. It is natural to suppose that the average electronic distribution is

intimately related to the electrostatic fields just mentioned, and possesses approximately the same characteristics. The physical properties of methane, such as low boiling-point and general similarity to a perfect gas, indicate not only that the nuclei are symmetrically placed but also that the electronic distribution is highly symmetrical. Accordingly, the following assumptions seem justified. In first approximation the average electronic distribution possesses a spherical symmetry about the carbon particle which is not altered by the infinitesimal displacements of the particles. Each hydrogen particle is acted upon by only two sorts of forces, electrostatic repulsions from the remaining hydrogen particles directed along the edges of the tetrahedron, and forces directed toward the carbon due to the combined effect of the carbon nucleus and the electronic distribution.

This picture is only a first approximation since the presence of the hydrogen nuclei undoubtedly prevents the electrons from having an average distribution which is a function only of the distance from the carbon. As a second approximation it seems justifiable to suppose that, superimposed upon the spherical distribution of the first approximation, there exist lesser electronic distributions which possess spherical symmetry about each of the hydrogen nuclei. It is evident that either of these approximations leads to the conclusion that the fields of force are central about each nucleus, a conclusion whose validity, however, rests upon the assumption that for infinitesimal displacements the electrostatic fields do not interact so as to cause any appreciable distortion of the symmetrical distributions of electrons. It seems probable that such an assumption can be no more than a close first approximation, and it is to be expected that the observed data may deviate somewhat from any results based upon it.

Let the mutual displacements of the hydrogen particles relative to one another be denoted by $q_1, q_2, \ldots, q_6$, and the displacements of each of the hydrogens relative to the carbon by r_1, r_2, r_3, and r_4, respectively. In accordance with the assumption that the field of force surrounding each nucleus is central, the potential energy, following an arbitrary displacement of the particles, will have the following form where W_1 and W_2 are two unknown functions:

$$W=\sum_{1}^{6} W_1(q_i)+\sum_{1}^{4} W_2(r_i)\ .$$

Since the amplitude of vibration is considered to be infinitesimal, the potential energy may be developed and all terms above the second degree may be disregarded.

$$W=W_0-\left(\frac{\partial W_1}{\partial q}\right)_0\sum_1^6 q_i-\left(\frac{\partial W_2}{\partial r}\right)_0\sum_1^4 r_i+\tfrac{1}{2}\left(\frac{\partial^2 W_1}{\partial q^2}\right)_0\sum_1^6 q_i^2+\tfrac{1}{2}\left(\frac{\partial^2 W_2}{\partial r^2}\right)_0\sum_1^4 r_i^2 .$$

Of the four constants appearing in this expression only three are independent, for if the normal state is to be a position of equilibrium the following condition must be obeyed:

$$\left(\frac{\partial W_2}{\partial r}\right)_0=-\sqrt{6}\left(\frac{\partial W_1}{\partial q}\right)_0 .$$

In treating the normal vibrations of the model it will be convenient to disregard translation and rotation of the model as a whole. The system is then one of nine degrees of freedom, and nine independent co-ordinates are needed to describe its motion. Six of these may be chosen immediately as the mutual displacements along the edges of the tetrahedron $q_1, \ldots, q_6$. The three remaining co-ordinates will be chosen as the components of a vector R, representing the distance between the carbon and the center of gravity of the hydrogen particles. The components of this vector x, y, z, are measured in the directions indicated in Figure 1.

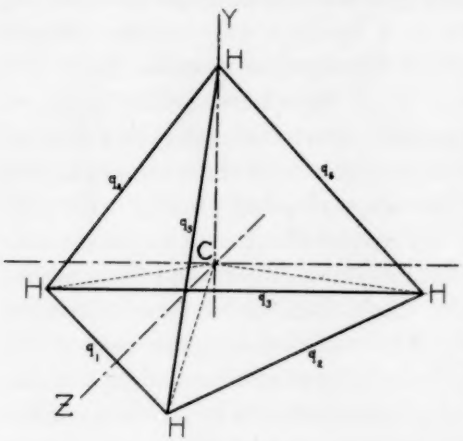

FIG. 1

In order to arrive at an expression for the potential and kinetic energies, each is set up as a general quadratic form in the nine variables and their time derivatives, respectively. The coefficients of these functions may be determined by considering special displacements where the energies may be simply computed. An example of such a special displacement is that for which the tetrahedron remains

regular and the center of gravity of the hydrogen particles remains fixed at the carbon, that is $q_1=q_2=\ \ldots\ =q_6$ and $x=y=z=0$.

By methods analogous to this, the following expressions for the energies were obtained where the potential energy is identical with the former expression transformed in terms of the new variables. Let the masses of the carbon atom and of each hydrogen atom be M and m, respectively, and let a be the normal length of a side of the tetrahedron.

Let

$$K_1=\left(\frac{\partial^2 W_1}{\partial q^2}\right)_0, \qquad K_2=\left(\frac{\partial^2 W_2}{\partial r^2}\right)_0, \qquad K'=\frac{-\sqrt{8}}{a\sqrt{3}}\left(\frac{\partial W_2}{\partial r}\right)_0,$$

and

$$\alpha=\frac{K_1}{K_2}, \qquad \beta=\frac{K'}{K_2}$$

$$T=\frac{m}{2}\Big\{\frac{4M}{4m+M}(\dot{x}^2+\dot{y}^2+\dot{z}^2)+\tfrac{5}{8}(\dot{q}_1^2+\dot{q}_2^2+\dot{q}_3^2+\dot{q}_4^2+\dot{q}_5^2+\dot{q}_6^2)$$
$$-2(\tfrac{1}{8})(\dot{q}_1\dot{q}_2+\dot{q}_1\dot{q}_3+\dot{q}_1\dot{q}_4+\dot{q}_1\dot{q}_5+\dot{q}_2\dot{q}_3+\dot{q}_2\dot{q}_5+\dot{q}_2\dot{q}_6+\dot{q}_3\dot{q}_4$$
$$+\dot{q}_3\dot{q}_6+\dot{q}_4\dot{q}_5+\dot{q}_4\dot{q}_6+\dot{q}_5\dot{q}_6)+2(\tfrac{1}{8})(\dot{q}_1\dot{q}_6+\dot{q}_2\dot{q}_4+\dot{q}_3\dot{q}_5)\Big\}$$

$$W=W_0+\frac{K_2}{2}\Big\{(\tfrac{4}{3}-\tfrac{8}{3}\beta)(x^2+y^2+z^2)+\Big(\alpha-\frac{\beta}{24}+\tfrac{5}{24}\Big)(q_1^2+q_2^2+q_3^2+q_4^2+q_5^2+q_6^2)$$
$$+2(\tfrac{1}{24})(1+\beta)(q_1q_2+q_1q_3+q_1q_4+q_1q_5+q_2q_3+q_2q_5+q_2q_6+q_3q_4+q_3q_6$$
$$+q_4q_5+q_4q_6+q_5q_6)-2(\tfrac{1}{8})(1+\beta)(q_1q_6+q_2q_4+q_3q_5)-2(\tfrac{1}{8})(1+\beta)(xq_1$$
$$-xq_2+xq_4-xq_6)-2\Big(\frac{2}{3\sqrt{6}}\Big)(1+\beta)(yq_1+yq_2+yq_3-yq_4-yq_5-yq_6)$$
$$+2\Big(\frac{1}{3\sqrt{3}}\Big)(1+\beta)(zq_1+zq_2-2zq_3-zq_4+2zq_5-zq_6)\Big\}.$$

These expressions may be treated in the usual manner for the determination of the normal modes of vibration, and it is found that the characteristic determinant may be written in the form:

$$(\mu-4\alpha-1)\Big(\mu-\alpha+\frac{\beta}{4}\Big)^2[\mu^3-2(\alpha-\tfrac{13}{16}\beta+\tfrac{5}{8})\mu+\tfrac{8}{9}\alpha-\tfrac{10}{9}\beta-\tfrac{16}{9}\alpha\beta-\tfrac{4}{9}\beta^2]^3=0.$$

While the system possesses nine degrees of freedom it is degenerate in that there are only four independent frequencies which occur

in the motion. These four normal frequencies, ν_1, ν_2, ν_3, and ν_4, are, respectively:

$$\frac{1}{2\pi}\sqrt{\frac{K_2}{m}}[4\alpha+1]^{\frac{1}{2}}, \qquad \frac{1}{2\pi}\sqrt{\frac{K_2}{m}}\left[\alpha-\frac{\beta}{4}\right]^{\frac{1}{2}},$$

$$\frac{1}{2\pi}\sqrt{\frac{K_2}{m}}[\alpha+\tfrac{5}{9}-\tfrac{1}{3}\tfrac{3}{6}\beta+\sqrt{(\alpha+\tfrac{5}{9}-\tfrac{1}{3}\tfrac{3}{6}\beta)^2-(\tfrac{8}{9}\alpha-\tfrac{1}{9}\tfrac{6}{}\alpha\beta-\tfrac{1}{9}\tfrac{0}{}\beta-\tfrac{4}{9}\beta^2)}]^{\frac{1}{2}},$$

$$\frac{1}{2\pi}\sqrt{\frac{K_2}{m}}[\alpha+\tfrac{5}{9}-\tfrac{1}{3}\tfrac{3}{6}\beta-\sqrt{(\alpha+\tfrac{5}{9}-\tfrac{1}{3}\tfrac{3}{6}\beta)^2-(\tfrac{8}{9}\alpha-\tfrac{1}{9}\tfrac{6}{}\alpha\beta-\tfrac{1}{9}\tfrac{0}{}\beta-\tfrac{4}{9}\beta^2)}]^{\frac{1}{2}}.$$

Denoting the roots of the determinant by μ_1, μ_2, μ_3, and μ_4, respectively, the kinetic and potential energies may be written in terms of four variables.

$$T=\frac{m}{2}[\dot{x}_1^2+\dot{x}_2^2+\dot{x}_3^2+\dot{x}_4^2]$$

$$W=\frac{K_2}{2}[\mu_1x_1^2+\mu_2x_2^2+\mu_3x_3^2+\mu_4x_4^2]$$

where

$$x_i=C_i\cos(2\pi\nu_i t+\gamma_i).$$

A direct application of the quantum theory shows that the amplitude of the ith normal co-ordinate may have only certain discrete values given by the equation,

$$C_i^2=\frac{n_i h}{2\pi^2 m\nu_i},$$

where h is the Planck constant and n_i a positive integer.

In order to study the motion belonging to each type of normal vibration it will be convenient to express the original co-ordinates $q_1, \ldots, q_6, x, y, z$, in terms of the new co-ordinates x_1, x_2, x_3, x_4. As is well known, the functions are linear and of the type

$$q_k=\sum_{i=1}^{i=4}B_{k_i}x_i.$$

Below is given a table of values for B_{k_i}, in terms of certain arbitrary initial constants made necessary by the existence of multiple roots in the determinant.

TABLE I

	x_1	x_2	x_3	x_4
q_1	$\sqrt{\frac{2}{3}}$	a	D_1	E_1
q_2	$\sqrt{\frac{2}{3}}$	$b-a$	D_2	E_2
q_3	$\sqrt{\frac{2}{3}}$	$-b$	D_3	E_3
q_4	$\sqrt{\frac{2}{3}}$	$b-a$	$-D_2$	$-E_2$
q_5	$\sqrt{\frac{2}{3}}$	$-b$	$-D_3$	$-E_3$
q_6	$\sqrt{\frac{2}{3}}$	a	$-D_1$	$-E_1$
x	0	0	$-\frac{2}{3}\frac{(1+\beta)(D_1-D_3)}{(3\mu_3-\frac{4}{3}+\frac{8}{3}\beta)}$	$-\frac{2}{3}\frac{(1+\beta)(E_1-E_2)}{(3\mu_4-\frac{4}{3}+\frac{8}{3}\beta)}$
y	0	0	$-\frac{4}{3\sqrt{6}}\frac{(1+\beta)(D_1+D_2+D_3)}{(3\mu_3-\frac{4}{3}+\frac{8}{3}\beta)}$	$-\frac{4}{3\sqrt{6}}\frac{(1+\beta)(E_1+E_2+E_3)}{(3\mu_4-\frac{4}{3}+\frac{8}{3}\beta)}$
z	0	0	$\frac{2}{3\sqrt{3}}\frac{(1+\beta)(D_1+D_2-2D_3)}{(3\mu_3-\frac{4}{3}+\frac{8}{3}\beta)}$	$\frac{2}{3\sqrt{3}}\frac{(1+\beta)(E_1+E_2-2E_3)}{(3\mu_4-\frac{4}{3}+\frac{8}{3}\beta)}$

where

$$a^2+b^2-ab=\tfrac{1}{4}\ ,$$

and

$$\left[1+\frac{8(1+\beta)^2}{3(3\mu_3-\frac{4}{3}+\frac{8}{3}\beta)^2}\right][D_1^2+D_2^2+D_3^2]=1\ ,$$

$$\left[1+\frac{8(1+\beta)^2}{3(3\mu_4-\frac{4}{3}+\frac{8}{3}\beta)^2}\right][E_1^2+E_2^2+E_3^2]=1\ .$$

Since each normal mode of vibration may be considered as an independent Planck oscillator, it will be sufficient to examine each separately. Suppose x_1 alone to have a value. Then $q_1=q_2=\ \ldots\ .$ $=q_6$ and $x=y=z=0$. The motion is clearly such that the hydrogen particles always lie at the corners of a regular tetrahedron while the carbon remains at the centroid. If x_2 alone is supposed to have a value, it is seen that the center of gravity of the hydrogen particles must remain fixed at the center of gravity of the system since $x=y$ $=z=0$. Moreover, a certain relation exists among the q's which may be shown to be the condition that the hydrogen particles move on the surface of a sphere. This might have been surmised from the fact that ν_2 does not contain the constant K_2. μ_2 is a double root of the determinant, and two arbitrary initial constants appear, one in the constants B_{k_i} and the other in the phase constant γ_2. The

motion is such that each of the hydrogen particles moves on an ellipse whose eccentricity and the direction of whose major axis are arbitrary.

In the motions corresponding to ν_3 and ν_4, the values of B_{k_i} and implicitly those of γ_i impose the condition that the motion shall be isotropic in three dimensions. The carbon particle moves on an ellipse, whose plane, whose eccentricity, and the direction of whose major axis are determined by the four arbitrary initial constants entering from the fact that μ_3 and μ_4 are each triple roots of the characteristic determinant. A detailed picture of the motion of any particle in these modes of vibration may be easily found by examining the coefficients of the linear equations given in the foregoing table. The Planck oscillator corresponding to ν_2 is one of two dimensions while that corresponding to either ν_3 or ν_4 is of three dimensions. It is evident that these higher dimensional Planck oscillators are entirely similar to the simple oscillator since neither the frequency nor the energy are dependent upon the initial constants defining the paths of the particles.[1]

The isotropic character of the vibrations ν_3 and ν_4 is due essentially to the simplifying conditions which have been imposed upon the model. In the real molecule where the motion is finite and anharmonic and where rotation reactions play an important rôle, it seems evident that the system will not be degenerate but that extra quantum conditions will determine the form of path along which the particles move as well as its orientation relative to the molecule. While it is not possible to determine these conditions from a consideration of the simplified model, the fine structure of the methane bands found by Dr. Cooley indicates their nature. Thus, if the carbon particle moves on an ellipse of eccentricity very different from unity, an internal angular momentum will be produced during transition which would cause certain discontinuities to appear

[1] On the basis of classical electrodynamics the intensity of radiation of an electrified particle moving harmonically on an ellipse depends, to a high approximation, upon the sum of the squares of the semi-major and semi-minor axes. It may be shown for the model under consideration that the family of ellipses on which each particle may move obeys the condition that this sum is constant. This indicates that if the electric moment depends upon the distance from the carbon nucleus to the center of gravity of the hydrogen nuclei, as will later be shown probable, the intensity of radiation is independent of the initial constants referred to above.

in the fine structure. These discontinuities are not found experimentally in the bands to be correlated with the vibrations ν_3 and ν_4, and the assumption is accordingly made that the particles move approximately along straight lines whose orientation relative to the molecule is determined, although at present unknown. While this assumption seems to be made necessary for a consideration of the fine structure, it is in no way essential to the remaining portion of the work, although it will be found to be convenient in determining the relative intensities of the bands.

3. CORRELATION OF THE NORMAL FREQUENCIES WITH THE OBSERVED FUNDAMENTAL FREQUENCIES

According to the work of Dr. Cooley, the infra-red absorption spectrum of methane consists of two very intense bands at 3.3 μ and 7.7 μ, and a considerable number of much fainter bands lying in the region from 2 μ to 8 μ. A table of the positions of the centers of these bands in waves per centimeter is given below. The experimental method is such as to give little exact information as to the relative intensities of the bands. Study of Dr. Cooley's original data, however, in conjunction with the earlier work of W. W. Coblentz[1] has yielded a series of values for the relative absorption coefficients which will serve as an indication of the order of magnitude of these quantities. It is noticed that many of the faint bands may be considered as combination bands. A system of combination relations is given in terms of four fundamental frequencies, and the computed frequencies are derived from these relations.

TABLE II

Frequency Obs.	Intensity	Identification	Computed Frequency
1304	50	ν_4	.....
Region not investigated	.....	ν_2	1520
2600	0.07	$2\nu_4$	2608
2824	0.5	$\nu_2+\nu_4$	2824
3014	20.	ν_3	.....
4122	0.1	$\nu_2+2\nu_4$	4128
4217	1.0	ν_1	.....
4315	0.7	$\nu_3+\nu_4$	4318
4543	0.2	$\nu_2+\nu_3$	4534

[1] "Investigations of Infra-Red Spectra," *Publications of the Carnegie Institute of Washington, D.C.*, No. 35, Part I, 1905.

Arithmetically there can be no unique choice of fundamental frequencies, providing difference combinations are allowed, but it may be shown that four and no more than four independent frequencies are needed to describe the methane bands. The very great intensity of the bands at 1304 and 3014 indicates that they must be considered to be fundamental. The band at 4217 is the strongest of the remaining bands, and since it cannot be derived from the other frequencies, it may be chosen as a fundamental frequency. The region about 1500 has not as yet been investigated by Cooley,

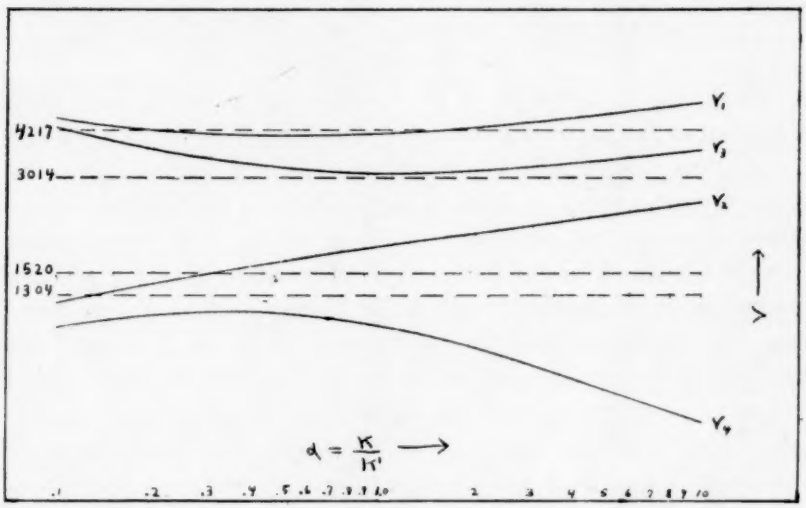

FIG. 2

and it may appear unsafe to place one of the frequencies here. The only remaining choice would be the band at 2824. If this were chosen as fundamental, the band at 4543 could only be derived from a combination of the sort

$$3014+2824-1304=4534.$$

Such a combination, however, would be very improbable since it involves a triple and also a difference combination. It is found that this band is not vanishingly faint, thus disproving the validity of the foregoing choice and making the first alternative of assuming a fundamental band to exist at 1520 seem preferable. It is noticed that the combination and harmonic bands are of very slight inten-

sity, and that they fall very close to the positions predicted by the combination relations. These two facts seem to indicate that the amplitude of vibration is small, and that it may be treated as infinitesimal without introducing any serious errors.

It appears that the methane spectrum consists essentially of four fundamental frequencies, and the question arises as to whether they may be correlated with the four normal frequencies of the simplified model. Such a correlation is greatly simplified through a consideration of the intensities of the bands, for, as has been seen, two of the theoretical frequencies, ν_1 and ν_2, are symmetrical, and hence their intensities should be very much less than those of the non-symmetrical frequencies ν_3 and ν_4. The bands experimentally observed at 3014 waves per centimeter and 1304 waves per centimeter are by far the most intense, and may be immediately identified with the theoretical frequencies ν_3 and ν_4, respectively. From the form of the functions it is moreover evident that in the region under consideration the frequency ν_1 is considerably larger than ν_2, and hence these frequencies are to be correlated with the bands at 4217 and 1520, respectively. The theoretical frequencies depend upon three constants, K_1, K_2, and K', or the ratios of the frequencies depend on the two constants α and β. A large number of graphs, of the ratios of the frequencies as a function of α, were made for a series of different values of β, and in this way the behavior of the functions was studied. If in the methane molecule the electronic configuration possesses a central symmetry about the carbon, the only forces acting between the hydrogen particles are Coulomb repulsions, and in this case $\beta = -2\alpha$. On the other hand, if there are also electronic configurations symmetrical about each of the hydrogen particles, it is evident, in general, that $|\beta| < |2\alpha|$ and in the limit β has the value of zero. It was found that for no values of the constants does there exist an exact correlation, but that the two sets of frequencies may be made to agree quite approximately in a region where β is very small. (It was thought that perhaps the faint bands at 4217 and 1520 might not be fundamental, but might rather be combination bands between the symmetrical and non-symmetrical frequencies; an examination, however, showed that if this were the case there could be no agreement between the experimental and theoretical frequencies.)

In the following table, values have been chosen for the constants such that the errors in agreement seem to be a minimum. Since the region of approximate correlation is fairly large, it is not to be expected that the absolute values of the constants are very accurate from the point of view of an exact description of the methane molecule.

$$K_1 = 13.15 \times 10^4$$
$$K_2 = 37.6 \times 10^4$$
$$K' = 2.44 \times 10^4$$

TABLE III

Observed Frequencies	Computed Frequencies	Per Cent Error
4217	3920	−7.1
1520	1532	+0.8
3014	3190	+5.9
1304	1304	0

From the high degree of symmetry of the normal methane molecule it seems justifiable to suppose that for slow nuclear vibrations, the magnitude of the electric moment will depend upon the distortion of this symmetry. The dissymmetry of the molecule is measured by the absolute value of R, the vector from the center of gravity of the hydrogen particles to the carbon. This assumption is, moreover, quite in agreement with the picture of the simplified model where each of the nuclei coincides with an effective charge due to the symmetrical distributions of electrons, thus making the electric moment proportional to R.

Table I shows that for the vibrations ν_1 and ν_2 the amplitude of R is zero, and hence the intensity of radiation should be zero. This appears, as has been said, to be entirely in accord with the foregoing correlation, for while the bands corresponding to ν_3 and ν_4, where R is not zero, are very intense indeed, the bands ν_1 and ν_2 are very faint, of the same order of intensity as the combination bands. It is interesting to compute the ratio of the intensities of ν_3 and ν_4. If A_0^i is the probability of spontaneous transition from the state corresponding to a frequency ν_i to the vibrationless state, then, as is well known by a formal comparison of the quantum theory with the classical theory,

$$A_0^i \nu_i = \frac{8}{3} \pi^2 \nu_i^4 ,$$

where g is a constant and a_i is the amplitude of vibration of the electric moment. The amplitude of R for the vibrations in question may be found from the constants of Table I, and by substitution one obtains

$$\frac{A_0^3\nu_3}{A_0^4\nu_4}=\left(\frac{\nu_3}{\nu_4}\right)^3\frac{(3\mu_4-\frac{4}{3}+\frac{8}{3}\beta)^2+\frac{8}{3}(1+\beta)^2}{(3\mu_3-\frac{4}{3}+\frac{8}{3}\beta)^1+\frac{8}{3}(1+\beta)^2}\,.$$

Substituting the values of the constants K_1, K_2, and K', previously used in determining the theoretical frequencies, we obtain

$$\frac{A_0^3\nu_3}{A_0^4\nu_4}=\left(\frac{\nu_3}{\nu_4}\right)^3\frac{1}{4\cdot 59}\cong 3\cdot 2\,.$$

Unfortunately, it is impossible to determine this ratio of intensities with any degree of accuracy from Dr. Cooley's data. Coblentz's curve shows these bands as narrow regions of unresolved absorption. It follows from the conceptions introduced by Einstein[1] that the integral of the absorption coefficient a_i over the absorption region should be proportional to $B_i^0\nu_i$, where B_i^0 is the probability coefficient of transition from the state zero to the state ν_i in a radiation field. In the case of methane, the absorption curves should be similar when plotted to the scale of frequencies since the form of such a curve depends upon the distribution of molecules in temperature equilibrium. It seems preferable to use the maximum value of a_i rather than the area under the curve, since Coblentz's data serve to determine the former with much greater certainty. By employing the well-known relations between the probability coefficients,[2] one obtains

$$\frac{A_0^3\nu_3}{A_0^4\nu_4}=\left(\frac{\nu_3}{\nu_4}\right)^3\frac{g_4}{g_3}\frac{a_3}{a_4}\,,$$

where g_3 and g_4 represent the a priori probabilities of the states ν_3 and ν_4. These a priori probabilities will be equal since μ_3 and μ_4 are each triple roots of the determinant mentioned previously. Substituting the data found by Coblentz, one obtains

$$\frac{A_0^3\nu_3}{A_0^4\nu_4}\cong\left(\frac{\nu_3}{\nu_4}\right)^3\left(\frac{1}{2\cdot 5}\right)\cong 5\,.$$

[1] Füchtbauer, *Physikalische Zeitschrift*, **21**, 322, 1920.

[2] A. Einstein, *ibid.*, **18**, 121, 1917.

The agreement between this value and the theoretical one seems to be well within the limits of uncertainty. An exact check could not be expected, but the comparison lends some support, at least, to the preceding work.

It may be well to summarize briefly the results of this section. A model representing the molecule of methane has been considered which obeys the following conditions. In the normal state four hydrogen particles lie at the corners of a regular tetrahedron while a carbon particle lies at the centroid. It is assumed that the amplitude of vibration is infinitesimal and that the fields of force possess a central symmetry about each particle. In a radiation field it is predicted that four fundamental frequencies may be absorbed, two of them very faintly and two very intensely. By means of three constants these four frequencies may be correlated quite closely with the observed spectrum of methane, both as to the positions of the bands and as to their relative intensities. That no exact agreement is found is quite in accordance with the approximate character of the assumptions. The values of the constants show that the effect on the frequencies of the forces between the particles is much less than the effect of the first derivatives of the forces, and that hence there exist electronic configurations surrounding the hydrogen nuclei, neutralizing to a considerable extent the electrostatic repulsions between these nuclei.

The analysis which has been developed may also be applied to the molecule of carbon tetrachloride. While it is possible to predict the general characteristics of this spectrum, it is not possible to determine with certainty the three constants entering the theoretical expressions. As in the case of methane, the simplified model of carbon tetrachloride yields four fundamental frequencies of which only two involve a motion of the carbon relative to the center of gravity of the chlorines. The spectrum of carbon tetrachloride, as observed by W. W. Coblentz,[1] consists of two intense bands at 6.5 μ and 13 μ, together with a number of much fainter bands. It is not possible at present to analyze these fainter bands uniquely, as in the case of methane, and hence to determine the three theoretical constants. In analogy to methane, however, it may be assumed that the value

[1] *Loc. cit.*

of the constant K' is small as compared with the constant K_2, and the positions of the two intense bands may be used to determine the following values for K_1 and K_2. It is found that these values predict a ratio of intensities for the bands in question which seems to be consistent with Coblentz' observations.

$$K_1 = 229 \times 10^4$$
$$K_2 = 30.4 \times 10^4$$

4. THE FINE STRUCTURE OF THE METHANE BANDS

Dr. Cooley has been able to resolve the bands corresponding to ν_3 and ν_4 into a series of regularly spaced sharp lines. The general form of the fine structure seems to show that each band possesses a positive, a negative, and a zero branch of the kind so often observed in the visible and ultra-violet spectra. When the moment of inertia is computed in the well-known manner from the difference in frequency between successive lines near the center of the band, it is found that the moment of inertia as determined from the ν_4 band is nearly twice that determined from the ν_3 band. The chemical and physical properties of methane make it extremely unlikely that methane could have two moments of inertia as widely different as these. It may, moreover, be shown from the general properties of rigid-body motion that unless the principal moments of inertia are exact multiples of the smallest one, the methane bands cannot consist of regularly spaced sharp lines. Thus, from chemical evidence we may be certain that the ellipsoid of inertia must be approximately spherical, and from the general character of the fine structure, as observed by Cooley, we may conclude that the principal moments of inertia cannot be different by more than 1 per cent. Since the spacing in the ν_3 band is about twice that in the ν_4 band, it is natural to wonder if the ν_4 band may not be composed of two systems of lines spaced midway between each other. A mechanism for such a result will be sought in the assumption that the methane molecule possesses a resultant electronic momentum which is fixed in direction in the molecule. The theory developed by H. A. Kramers[1] may be very simply applied to the methane molecule.

Since the three principal moments of inertia, A, B, and C, are equal, the total electronic momentum S may be supposed without

[1] *Zeitschrift für Physik*, **13**, 343, 1923.

loss of generality to be directed along the A axis. With the approximations made by Kramers, the total angular momentum and the total rotational energy are given by the equations

$$J^2=P^2+Q^2+R^2$$
$$2EA=(P-S)^2+Q^2+R^2,$$

where P, Q, and R are the components of total angular momentum along the principal axes. The quantum conditions defining the stationary states are very simple since the system is one possessing an axis of symmetry,

$$J=\frac{mh}{2\pi}, \qquad P=\frac{nh}{2\pi}.$$

By letting $S=sh/2\pi$, where s is the number of units of electronic momentum, the rotational energy may be expressed simply by

$$E=[m^2-2ns+s^2]\frac{h^2}{8\pi^2A}.$$

If the energy is expressed in terms of the canonical momenta, $I_m=mh$ and $I_n=nh$, the angle variable w_m and w_n conjugate to them may be found by partial differentiation:

$$\frac{\partial E}{\partial I_m}=\frac{dw_m}{dt}=\omega_m=\frac{I_m}{4\pi^2A}$$
$$\frac{\partial E}{\partial I_n}=\frac{dw_n}{dt}=\omega_n=-\frac{sh}{4\pi^2A}.$$

The frequency of radiation absorbed or emitted will be

$$\nu=\frac{E''-E'}{h}\cong\omega_m(m''-m')+\omega_n(n''-n').$$

In order to find the selection rules for the numbers m and n, it is necessary to notice that on the basis of classical mechanics the motion consists of a rotation about A with the frequency ω_n and a precession about J with the frequency ω_m. Suppose that the electric moment vibrates harmonically with frequency ω_0 along a line through the center of gravity of the molecule, so that its projections on the A, B, and C axes are given by $\alpha\cos(2\pi\omega_0 t+\delta_0)$, $\beta\cos(2\pi\omega_0 t+\delta_0)$, and o, respectively. Let there be a rectilinear co-ordinate system, x, y, z, fixed in space, whose x axis coincides with the invariable

axis J. It may be very simply shown that the projections of the electric moment on these axes are given by the following expressions, where $\cos\theta = P/J$:

$$x = a\cos\theta\cos(2\pi\omega_0 t+\delta_0) + \frac{\beta\sin\theta}{2}\{\cos[2\pi(\omega_0+\omega_n)t+\gamma_1]+\cos[2\pi(\omega_0-\omega_n)t+\gamma_2]\},$$

$$y = \frac{a\sin\theta}{2}\{\cos[2\pi(\omega_0+\omega_m)t+\gamma_3]+\cos[2\pi(\omega_0-\omega_m)t+\gamma_4]\},$$

$$-\frac{\beta(\cos\theta+1)}{4}\{\cos[2\pi(\omega_0+\omega_m+\omega_n)t+\gamma_5]+\cos[2\pi(\omega_0-\omega_m-\omega_n)t+\gamma_6]\}$$

$$-\frac{\beta(\cos\theta-1)}{4}\{\cos[2\pi(\omega_0+\omega_m-\omega_n)t+\gamma_7]+\cos[2\pi(\omega_0-\omega_m+\omega_n)t+\gamma_8]\},$$

and a similar expression for z.

These expressions, by an application of the correspondence principle, lead to the following selection rules, k being the quantum number defining the vibration.

a) The electric moment vibrates along a line which is neither parallel nor perpendicular to the axis of electronic momentum.

$$a\neq 0, \quad \beta\neq 0.$$

$$\begin{cases}\Delta k=1\\ \Delta m=0\\ \Delta n=0\end{cases}\quad\begin{cases}\Delta k=1\\ \Delta m=0\\ \Delta n=\pm 1\end{cases}\quad\begin{cases}\Delta k=1\\ \Delta m=\pm 1\\ \Delta n=0\end{cases}\quad\begin{cases}\Delta k=1\\ \Delta m=\pm 1\\ \Delta n=\pm 1\end{cases}$$

b) The electric moment vibrates along a line parallel to the electronic momentum.

$$a\neq 0, \quad \beta=0.$$

$$\begin{cases}\Delta k=1\\ \Delta m=0\\ \Delta n=0\end{cases}\quad\begin{cases}\Delta k=1\\ \Delta m=\pm 1\\ \Delta n=0\end{cases}$$

c) The electric moment vibrates along a line perpendicular to the electronic momentum.

$$a=0, \quad \beta\neq 0.$$

$$\begin{cases}\Delta k=1\\ \Delta m=0\\ \Delta n=\pm 1\end{cases}\quad\begin{cases}\Delta k=1\\ \Delta m=\pm 1\\ \Delta n=\pm 1\end{cases}$$

The frequencies of radiation resulting from a change in vibrational and rotational state may be divided into the following classes of lines:

$$\text{Class I} \quad \begin{cases} m \to m \pm 1 \\ n \to n \pm 1 \end{cases} \qquad \nu = \nu_0 + (\pm 2m + 1 \mp 2s)\frac{h}{8\pi^2 A}$$

$$\text{Class II} \quad \begin{cases} m \to m \pm 1 \\ n \to n \end{cases} \qquad \nu = \nu_0 + (\pm 2m + 1)\frac{h}{8\pi^2 A}$$

$$\text{Zero branches} \quad \begin{cases} m \to m \\ n \to n \end{cases} \qquad \nu = \nu_0$$

$$\begin{cases} m \to m \\ n \to n \pm 1 \end{cases} \qquad \nu = \nu_0 \mp \frac{(2s)h}{8\pi^2 A}.$$

In general, it is seen that Class II lines form an equally spaced series of single lines, but that Class I forms a series of doublets, each doublet being placed symmetrically about one of the Class II lines. If s is equal to an integral number, the doublets of Class I coincide

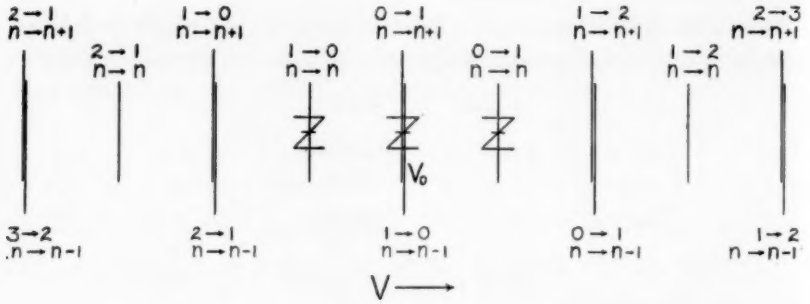

FIG. 3

with the lines of Class II; but when $s=\frac{1}{2}$, the doublets of Class I again fall together, but this time midway between the Class II lines. This seems to offer an explanation of the band ν_4. Above (Fig. 3) are plotted a few of the lines theoretically to be expected when $s=\frac{1}{2}$. The lines marked with a z are the positions of the zero branches where $\Delta m = 0$.

A study of the experimental intensities of the band ν_3 seems to indicate that the lines of Class I are systematically stronger than those of Class II. This is quite uncertain, however, since the experi-

mental method does not serve to determine the intensities accurately but only the positions of the lines. By dividing the lines into these two classes, the moment of inertia of the molecule may be computed from either set of lines to be about 5.1×10^{-40} gm cm^2. The moment of inertia as computed from the band ν_3 was 5.66×10^{-40} gm cm^2. Such a discrepancy cannot be wholly due to the same type of reaction between vibration and rotation which is found in the infra-red spectra of the halogen halides since the quadratic term in the line formula is relatively small. In connection with the comparison of these two bands, the question arises as to why only one class of lines is apparently observed in the band ν_3. This cannot be answered completely, but it may well be that the carbon vibrates along lines which have different orientations with respect to the axis of electronic momentum. Thus, for the band ν_4, a and β may be of the same order of magnitude, while for the band ν_3, β is perhaps much smaller than a. The present work does no more than attempt to show that the essential features of the fine structure indicate that the molecule of methane possesses an internal electronic angular momentum of amount $\frac{1}{2}(h/2\pi)$. A complete understanding of the fine structure must rest upon a more general discussion of the problem of interaction between vibration and rotation for a molecule of this sort.

UNIVERSITY OF MICHIGAN

TESTS OF SPECTROSCOPIC PARALLAXES AND ABSOLUTE MAGNITUDES BY DOUBLE STARS

By G. SHAJN

ABSTRACT

To test the accuracy of the spectroscopic methods for determining absolute magnitudes and parallaxes by the criterion that $\Delta M - \Delta m = 0$, 194 double stars were examined. Fifty-five were of late, and 139 of earlier, spectral types.

The *derivation of M for later spectral types* is found satisfactory, the value of $\Delta M - \Delta m$ being between ± 0.28 and ± 0.48, which corresponds to an accuracy in the parallax of 14 to 25 per cent of the parallax itself. For spectral types A and B, the accuracy is considerably less, the average value of $\Delta M - \Delta m$ ranging between ± 1.08 and ± 1.24, corresponding to 65–77 per cent of the parallax itself.

The correlation between spectral type and absolute magnitude for the A and B stars is evident for such stars in moving clusters, but much less evident for individual stars of known trigonometric parallax. These stars show very large deviations from the reduction curve and a considerable dispersion of M.

The accuracy with which absolute magnitudes are being determined by spectroscopic methods depends on the precision (1) of the trigonometric parallaxes of all stars entering into the reduction curves; (2) of the determination of intensities of spectral lines in stars of later types; (3) of the estimation of the spectral subdivisions of early types; and, finally, it depends on the generality of those empirical correlations in stellar spectra on which the methods are based. It is especially important to select for the reduction curves such stars as do not represent special cases. The number of stars for which the trigonometric method gives reliable parallaxes is limited, although more and more are becoming available. This is especially true of stars belonging to spectral types A and B. Therefore it is important to use an independent way for testing the accuracy of the absolute magnitudes and parallaxes determined by the spectroscopic process.

It appears to me that physically connected double stars are excellent material for such an investigation. It is evident that in systems which show orbital motion or common proper motion, the difference between the apparent magnitudes of the components Δm should be equal to the difference of their absolute magnitudes ΔM:

$$\Delta M - \Delta m = 0 . \qquad (1)$$

Properly we should consider here the bolometric magnitudes of the stars, but equation (1) remains true if the absolute and the apparent magnitudes are referred to the same visual system. It is evident that this equation does not depend on the parallax of the double star or on the value of Δm. This simple condition is therefore a criterion for the accuracy of spectroscopic methods. I have applied this equation separately to stars belonging to later spectral types and to those of spectral types A and B.

The list of 1646 spectroscopic parallaxes determined at the Mount Wilson Observatory by Adams, Joy, Strömberg, and Burwell[1] contains 55 double stars (of which two are triple systems), in which both components were used for the determination of their absolute magnitudes. All of these stars belong to spectral types not earlier than F or late A. Among these 55 pairs there are 22 pairs which had not been used by the authors for their reduction curves. For these 22 pairs the arithmetic mean of the difference $\Delta M - \Delta m = 0.28$. This is an excellent proof of the high accuracy of the spectroscopic parallaxes contained in this list. Considering all 55 pairs, we find that this arithmetic mean is 0.48. It appears that out of these 55 pairs, this difference ranges between 0.0 and 0.1 for 12; for 22 pairs, this difference is between 0.2 and 0.4; for 11 pairs, between 0.5 and 0.6; for 2 pairs, between 0.7 and 0.8; for 4 pairs, between 0.9 and 1.0; for one pair it is equal to 1.1, and for three pairs it is more than 1.1. The last three pairs are α Herculis ($\Delta M - \Delta m = +1.9$), γ Leonis ($\Delta M - \Delta m = -2.2$), and ϵ Hydrae AB–C ($\Delta M - \Delta m = -2.6$). The large differences in the three last-named stars are evidently due to the following causes.

In α Herculis the estimated spectrum of the brighter component is of type Mb, while its measured spectral type is G5. The determination of spectroscopic absolute magnitudes for stars of spectral type M and of absolute magnitude fainter than +2.0 is probably not very accurate. For instance, the average difference between the absolute magnitudes of the same 29 stars of spectral type M, as given in the Mount Wilson lists of 1920[2] and of 1917,[3] is $-1^{M}.12$.

[1] *Astrophysical Journal*, **53**, 13, 1921.

[2] *Ibid.*

[3] *Ibid.*, **46**, 313, 1917.

Evidently the spectral type of α Herculis, close to type M, explains the large deviation found in the case of this star.

γ Leonis belongs to a group of stars similar to 61 Cygni and has an unusually large proper motion of 0".338, with a trigonometric parallax of 0".000. It is exceedingly strange that the spectroscopic absolute magnitude of the brighter component of this star exceeds that of the fainter component, while at the same time $\Delta m = -1.2$. The spectroscopic parallax of the brighter component is 0".044, which is evidently too large, since it would otherwise have been determined by the trigonometric method.

The spectroscopic parallax of ϵ Hydrae AB is also too large. It is equal to 0".055, while the trigonometric method gives 0.015. The apparent magnitudes of the two components A and B are 4.0 and 5.0. It seems probable that the composite character of the spectrum of this star is responsible for its large value of $\Delta M - \Delta m$. A redetermination of the absolute magnitudes of these three stars would probably reduce their discrepancies. If these three stars are excluded, the arithmetic mean of $\Delta M - \Delta m$ becomes equal to 0.38 for the remaining pairs.

The authors themselves estimate the probable error of their spectroscopic absolute magnitudes as 0.40, which is in excellent agreement with the value found from the double stars. The probable error of a spectroscopic absolute magnitude for a star of spectral type later than F is, therefore, equal to nearly 20 per cent of the parallax itself.

For the determination of absolute magnitudes of stars of spectral types A and B, according to the method proposed by Adams and Joy[1], it is necessary to know the spectral subdivision of any given star and also the character of its spectral lines (nebulous or sharp). The first factor is by far the more important one. Accurate spectral types of both components of double stars belonging to classes A and B are available for 139 pairs, observed at the Harvard, Lick, and Mount Wilson Observatories.[2] By means of the reduction curve given by Adams and Joy, it was possible to derive the differences in the absolute magnitudes between the components of these double

[1] *Astrophysical Journal*, **56**, 242, 1922; **57**, 149, 1923.

[2] Leonard, *Lick Observatory Bulletin*, No. 343 (**10**, 169, 1923).

stars. It is admitted that some slight uncertainty is introduced in the results on account of the fact that for most of the stars employed the character of the spectral lines was unknown, and in all of these cases an average between *n* and *s* was assumed. However, the results of Adams and Joy prove that the influence of the character of the lines (nebulous or sharp) is not very large for A stars, and that it is almost negligible for stars from Bo to B5.

Figure 1 shows the relation between the values of ΔM and of Δm. The stars were divided into several groups according to the type of the earlier component. In each group the type of the later companion is taken as abscissa. The ordinates are the differences in magnitude, later minus earlier component. The circles represent the differences of the apparent magnitudes Δm, while the curves represent the differences in the absolute magnitudes ΔM, obtained from the reduction curves of Adams and Joy,[1] respectively for the *n* and *s* stars. It would, of course, be expected that the points follow more or less closely the curves. It will be seen at a glance that this is not the case. In fact, the agreement between the values of Δm and the curves is entirely unsatisfactory. Leonard's list contains 5 pairs in which one of the components has a composite spectrum. For these stars I have used average spectral types. Our 139 pairs include also 25 stars in which the spectral type of the companion is between F2 and F5. This introduces a very small extrapolation of the reduction curves which did not seem objectionable, and besides there are some indications that a considerable portion of the stars classified at Harvard and by Leonard as F5 are placed somewhat earlier at Mount Wilson. Most of these 25 pairs are very close double stars and are mainly taken from *Circulars of the Harvard College Observatory*, Nos. 178, 184, 196, and 221, and in part also from Leonard's list. The arithmetic mean of the difference $\Delta M - \Delta m$ for all 139 pairs is 1.24. If the 25 pairs mentioned above are excluded, we find for the remaining 114 pairs a mean of 1.08.

It should be noted that for saving space the values corresponding to spectral types later than F2 have been placed in the drawings in Figure 1 under the same abscissa as spectral type F2. It was legitimate to do this, since the curves are in all cases approximately

[1] *Astrophysical Journal*, **57**, 297, 1923, Table I; *ibid.*, **56**, 248, 1922, Table V.

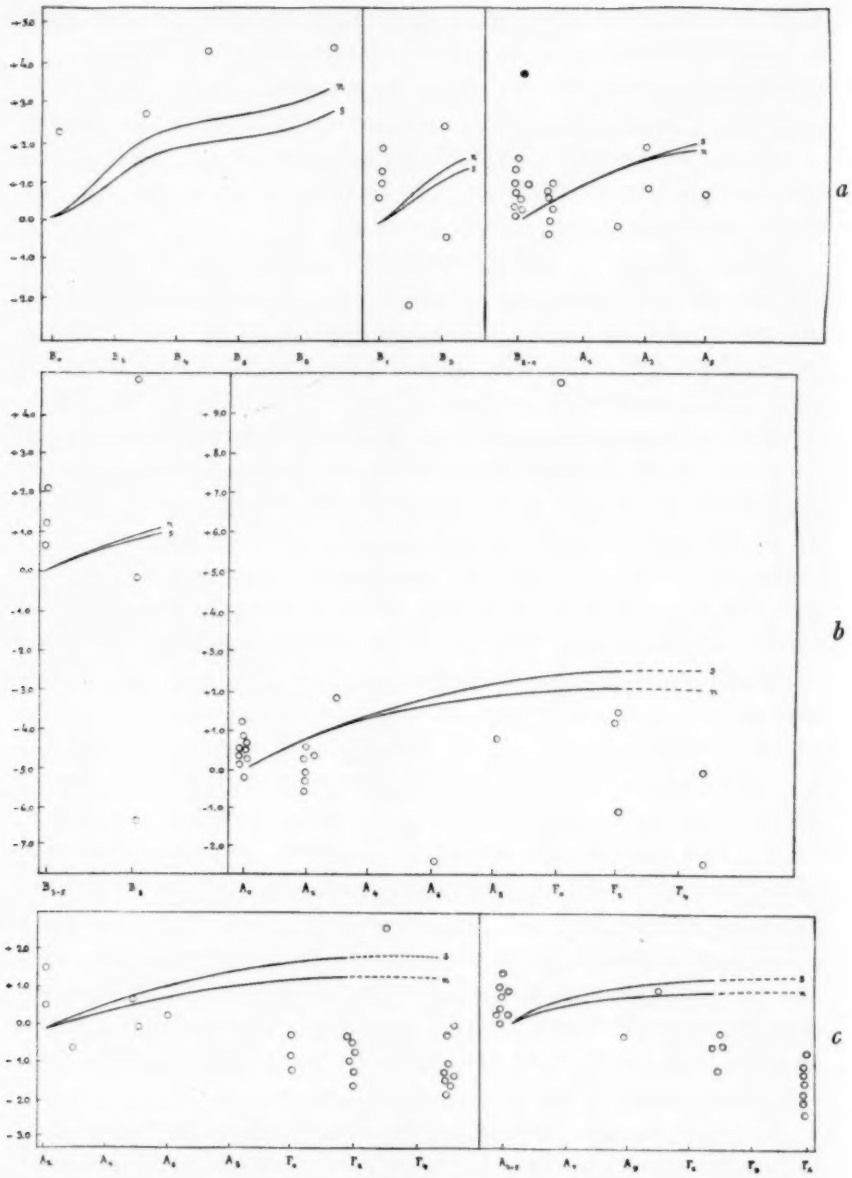

FIG. 1

horizontal, beginning from spectral type Fo. Some of the groups are not shown in the drawing, but their general character remains the same.

We find, therefore, that the mean difference $\Delta M - \Delta m$ for A and B stars is somewhere in the neighborhood of 1.08 or 1.24, while for stars of later types this difference was as small as 0.28 or 0.48. In other words, for A and B stars, the average error of a spectroscopic parallax amounts to as much as 56 to 77 per cent of the parallax itself. Individual stars give evidently still larger discrepancies. Among our 139 pairs, there are 43 pairs for which the value of $\Delta M - \Delta m$ exceeds $1^{M}.5$. Accordingly, for these stars, the average error of the parallaxes is more than 100 per cent of the parallax itself. The fact that the spectral subdivisions of the Harvard, Mount Wilson, and Lick observatories do not exactly correspond cannot be responsible for these large discrepancies, since we consider here only the differences between the spectral types of the two components.

The double stars seem to indicate, therefore, that the accuracy with which spectroscopic parallaxes are determined for A and B stars is roughly one-third that for stars of later types, and one out of three early-type stars will have an error of over 100 per cent in its spectroscopic parallax.

Unfortunately, I was not able to apply the double-star test to the methods used by Edwards[1] and by Lindblad[2] for the determination of absolute magnitudes of early-type stars, since there are no corresponding data for double stars.

The principle used in the method for deriving absolute magnitudes of stars of later spectral types finds a strong support in Saha's theory of ionization and in modern views on stellar evolution. This cannot be said of the method used by Adams and Joy for stars of types A and B. There is of course no doubt that the correlation established by the two investigators is true in a general way and that it enables them to derive absolute magnitudes for the average of sufficiently large numbers of stars. But it does seem doubtful that this simple correlation between spectral type and absolute magnitude remains correct for each individual star. The increase in the absolute magnitudes from Bo to F2 is not in good accordance with

[1] *Monthly Notices*, **83**, 47, 1922. [2] *Astrophysical Journal*, **55**, 85, 1922.

the theory of Russell and Hertzsprung. The absolute magnitudes of two stars of type A9 of the same mass on the descending and ascending branches must be very different. According to Eddington's theory of radiative equilibrium, the bolometric magnitude of a giant is independent of its stage of evolution, and depends only on its mass. Therefore, the absolute magnitude of some stars of type A9 may be equal to that of stars of type Bo. Further, the method assumes a small dispersion in masses. There is little doubt that the relation between spectral type and mass will complicate the correlation established by Adams and Joy. Their reduction curves are based largely on stars belonging to moving clusters. It is possible that these stars are not representative of their corresponding spectral types. For example, the stars belonging to the Ursa Major cluster, and probably also those which belong to the Taurus group, are in most cases on the descending branch of stellar evolution.

To this we may add the following quotation from W. W. Campbell's *Stellar Motions*, p. 273:

> It is fairly well established that when the two spectra are substantially equal in brightness they are identical in class; and when one spectrum is considerably fainter than the other, the spectrum of the secondary is apparently of a slightly earlier class than the spectrum of the primary. There appear to be no exceptions to this rule.

The giant systems of visual double stars also show that the spectrum of the secondary is of earlier type than the spectrum of the primary.[1] This fact does not agree with the reduction curve of Adams and Joy. It is evident that the double stars are more representative for stars in general than the members of moving clusters, since among them we find both giants and dwarfs, while the known moving clusters are mainly composed of dwarfs.

Figure 2*b* shows the correlation between absolute magnitude and spectral type for stars belonging to moving clusters, and Figure 2*a* for stars not belonging to such clusters, but for which reliable trigonometric parallaxes are known. The circles indicate stars with diffuse lines, while the ⊖ indicates stars with sharp lines. For the members of moving clusters, represented in Figure 2*b*, the correlation

[1] Lau, Leonard, Doig, Abetti, and my unpublished observations of double stars by Seares' method of exposure ratio.

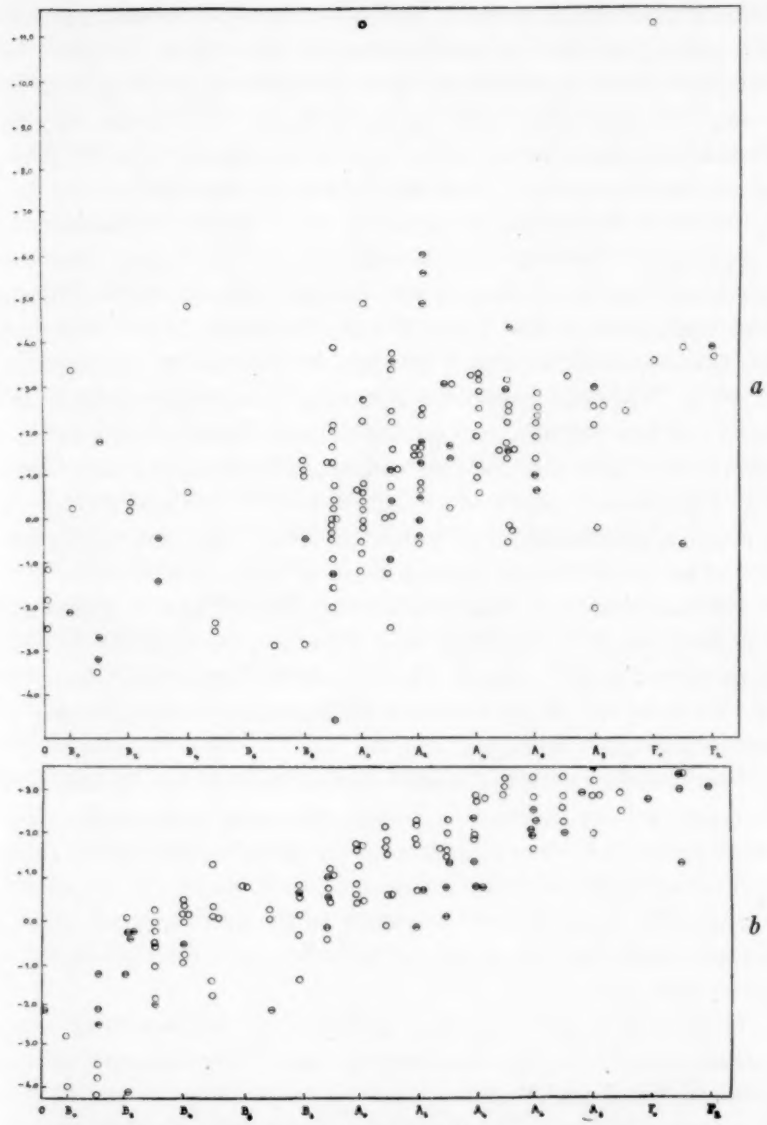

FIG. 2.—(*a*) Individual stars; (*b*) stars belonging to moving clusters.
○, stars with diffuse lines or with lines of unknown character.
⊖, stars with sharp lines.

between absolute magnitude and spectral type is unmistakable, confirming therefore the results obtained by Adams and Joy. For the other stars, represented in Figure 2*a*, this correlation is much less evident. There is apparently some indication that, on the average, the absolute magnitudes increase with advancing spectral types, but this relation is to a considerable extent masked by the very large dispersion of the individual values of the absolute magnitudes corresponding to the same spectral subdivision. One might think that this large dispersion is due to possible uncertainties in the trigonometric parallaxes of the A and B stars. However, it will be noticed that this dispersion is largest for stars situated in the upper part of Figure 2*a*. The parallaxes of these stars are comparatively large, as is shown by the formula $M=m+5+5 \log \pi$. Since m is never very large, it is evident that to large values of M correspond large values of π. The probable errors of the parallaxes of these stars are certainly much smaller than their parallaxes. For stars having negative or very small parallaxes, I have assumed the value of $+0''.005$ for the computation of absolute magnitudes. There is no doubt that some stars have values lower than this. Therefore some of the absolute magnitudes should be lower than shown in Figure 2*a*. This would tend to make the disagreement with the stars belonging to moving clusters still more striking.

Figure 2 supports the results obtained from the double stars. Therefore we are inclined to believe that spectroscopically determined values of M or of π for stars of spectral classes A and B should be accepted only with the greatest caution, although the average parallax of a group of stars belonging to the same spectral subdivision will doubtless be given correctly by the reduction curves of Adams and Joy.

Double stars will doubtless serve for the improvement of the methods now in use for the determination of absolute magnitudes, especially for A and B stars. They may also be employed to great advantage for giants for the study of possible relations between absolute magnitude and spectral characteristics. For this purpose a list of stars would be selected, having the primary component an M giant, and the secondary of a spectral type permitting an accurate determination of its spectroscopic absolute magnitude. Thus, it will

perhaps be possible to select a series of trustworthy standards for the determination of the absolute magnitudes of stars of M type. Unfortunately, such stars are not very frequent (α Herculis, α Scorpii, Innes G. C. 15^h72).

Figure 2 shows that it is very difficult to establish a definite change in absolute magnitude corresponding to such a small change in spectral type as that of one-tenth of one spectral class, even if we attempt only to derive an average value of the absolute magnitudes of a group of stars. However, for one-half or one-third of a spectral class, the phenomenon is quite distinct. Therefore it would seem justifiable to limit ourselves in some investigations to a determination of spectral types with an accuracy of approximately one-third of a spectral class. Limiting ourselves to this accuracy, we shall be able to use for the determination of absolute magnitudes, not the actual spectra, but the color indices of the stars, or, in general, any color equivalents of the white stars, thus extending the methods to the faint stars. By Seares' method of exposure ratios, for instance, it is easy to determine the color equivalents of white stars with an accuracy of one-half to one-third ot a spectral class, the color indices of such stars ranging from -0.30 to $+0.30$. By this method, we shall be able to determine with some degree of accuracy the distances of the remotest stars in our universe. It is evident that such knowledge will be of great value for various statistical investigations.

ASTRONOMICAL OBSERVATORY, PULKOVO
February 1924

A PHOTOMETRIC COMPARISON OF THE SOLAR CORONAS OF 1918 AND 1925

By JAKOB KUNZ and JOEL STEBBINS

ABSTRACT

Total light of solar corona.—The solar corona of January 24, 1925, was compared with three standard lamps by means of photo-electric cells. After allowance for the extinction of the earth's atmosphere, the total light of the corona is found to be nearly the same as measured on June 8, 1918 (Table VI), and there is no evidence of variation between sun-spot maximum and sun-spot minimum. The results are shown to be in good agreement with the bolometric measures of Abbot in 1908, and with the photo-electric measures of Briggs in 1922.

The brightness of sky near the sun was found to decrease 5300-fold during totality in 1918, and 5500-fold in 1925.

The results show the *usefulness of the photo-electric cell* for photometric measures of diffuse objects like the solar corona.

After the successful measurement of the corona of June 8, 1918, with a photo-electric cell,[1] it was our plan to repeat this observation in September, 1923, when the prospects for a good sky in California were very favorable. We therefore organized a second expedition and were at Catalina on the critical date, but in common with other observers we were frustrated by the presence of clouds.[2] The disappointment was particularly severe as the sun at that time was near the minimum of spot activity, whereas in 1918 it had been just past the sun-spot maximum. We had hoped to determine the total light of the corona by the same methods and with exactly the same instruments as before, and thus have evidence of any change through the sun-spot cycle.

The eclipse of January 24, 1925, did not promise very much for such a photometric comparison. As far east as New England the altitude of the sun would be only 17°, and even if the sky were what might ordinarily be called clear, it was too much to hope that the transparency would be good enough for a fair estimate of the atmospheric extinction. Nevertheless, as the date was still near sun-spot minimum, it seemed worth while to make the effort, since a similar opportunity would probably never come again; the next sunspot

[1] *Astrophysical Journal*, **49**, 137, 1919. *Popular Astronomy*, **26**, 665, 1918.

[2] *Popular Astronomy*, **32**, 18, 1924.

minimum would be perhaps sixteen or seventeen years after the original observations in 1918. The apparatus used in 1918 and again in 1923 was all intact, and it was expected to be an easy matter to make a quick trip to a favorable locality and secure the desired measures.

Although the path of totality crossed northern Wisconsin and Michigan, it was evident that no useful photometric measures could be made west of New York or Connecticut because of the low altitude of the sun. In making a selection of the site, care was taken that there would be freedom from the smoke of a large city. We were therefore very fortunate to have a cordial invitation from Professor Frederick Slocum to join the parties at the Van Vleck Observatory, of Wesleyan University, Middletown, Connecticut. The predicted duration of totality was 112 seconds, and it was evident that if we could locate in the Observatory itself there would be many advantages.

After shipping the apparatus in several boxes, we arrived at Middletown on January 18—six days before the eclipse. The first afternoon we were taken over the Observatory by Professor Slocum, who put everything at our disposal, and we were very glad to find that no one else had asked for the transit-room. In a few minutes we had removed a transit instrument from one of the piers, and there we had a pier for the galvanometers, a complete house, a place on the roof for the photometer tubes, and had already accomplished what would have been four or five days' work at an eclipse camp. Because of the wintry conditions, the thermometer going below zero Fahrenheit on some days, we were glad, indeed, to have this shelter. We first proposed to lead some wires up through the slit of the transit-room and connect with the photometer tubes on the roof. In fact, we spent a half-day building a platform and wind screen up above; but a heavy snowfall, the low temperature, and a high wind caused us to reconsider the plan. It was not so much the prospective discomfort of the observers that we had in mind as the fact that we were reluctant to introduce wide differences of temperature into the galvanometer circuits, and, moreover, for calibrating the photo-electric cells we were not sure that we could count on a cell keeping the same sensitivity in the moderately cool transit-room

and in the outside conditions. Therefore, it was with some relief that we found it was just possible to point the photometer tubes out the open south window of the room, and get both the sun and a clear space to one side.

We were somewhat surprised on the second morning to find that one express box shipped from Madison was missing. This box contained the equatorial mounting, the cell boxes, and some minor parts. The really delicate features of our installation, the galvanometers, cells, and standard lamps, had been carried as hand luggage, and, barring accidents, we would have been able to improvise some sort of a photometer, no matter what mishap should occur to the express shipment. After waiting twenty-four hours for the missing box, we started tracers by telegraph, but immediately decided to go ahead on the basis that the lost parts would not be found. This was just as well, for the box finally arrived at Middletown on eclipse day about ten minutes after totality. Substitute cell boxes were quickly made in a local planing mill, and much to our gratification the college mechanician was able to make shutters and do the other machine work necessary. Professor Slocum had available a 3-inch equatorial mounting on a tripod which was not to be used otherwise, and with this we had everything replaced. This setback of between one and two days, with less than six days at the station, was enough to be disconcerting, but the only real loss was that of the opportunity to visit and study better the preparations of our colleagues at Middletown.

Our program of measuring the corona by means of photo-electric cells exposed directly at the time of totality was the same as in 1918. We had a double-barreled arrangement, each of two cells with an effective aperture of 25 mm placed in a box at the lower end of a metal tube 100 mm in diameter and about 122 cm long. At the upper end of each tube was a diaphragm 89 mm in diameter at an effective distance of 127 cm from its corresponding cell. Any point on the cell was illuminated by a circle of sky with radius equal to 2°.0. The clear field of the apparatus, about 3°, would include all of the corona and allow for the motion of the sun during totality. There were, of course, diaphragms in each tube to prevent any side reflection to the cell.

The twin tubes on the equatorial mounting in 1918 were provided with a stop in declination which allowed just 8° motion. During totality the tubes were turned back and forth from the sun to the sky 8° north, thus getting a measure for the elimination of the sky background. In 1925 it was found necessary to shift, not north, but about northwest from the sun, in order to point the tubes at an unobscured sky from the window of our transit-room, and it was afterward found that the distance turned was slightly over 7°, which, however, was nearly the same as before. Each box with its cell could be attached to the equatorial mounting or placed on the photometer bench for measures of the standard lamps.

The electrical circuits were the same, batteries of small dry cells giving a total up to about 300 volts. Of the several galvanometers which were ready, we used two by Leeds and Northrup, one with a constant of 2×10^{-10} amperes for 1 mm deflection at 1-m scale distance, and the other about three times less sensitive. With damping shunts, the times to secure full deflection were slightly over 10 seconds and 6 seconds, respectively. Each galvanometer has a plane mirror, and was used with a view telescope with a scale distance of 2.5 m. As before, each circuit consisted of a battery, photoelectric cell, galvanometer, and guard resistance in series. Exposure of the cell to light gave the current to be measured by the galvanometer deflection.

We were fortunate in having still on hand the original cells used in 1918. The first, called K 59 Number 1, was operated by Mr. Stebbins, and the other was K 113 Number 2, with which the successful measures were secured by Mr. Kunz at Rock Springs. Each of these cells seems to have kept its characteristics without change. The only use they have had in the interval of nearly seven years was in the preparations for the eclipse of 1923. The curves of color-sensitivity are practically the same for the two cells, and they probably do not differ as much as do the eyes of different persons in this regard.

We also had on hand the same Hefner lamp and the two electric pyrometer lamps used in 1918 and 1923. Each lamp, N_1 and N_2, burned at 0.60 ampere, as determined with a precision ammeter at Madison; this corresponded to 3.80 and 3.50 volts, respectively, at

the terminals of the lamps. Our voltmeters were tested with a precision instrument in the Physics Laboratory at Wesleyan. The electric lamps had not been used for other purposes, and the standard candle was burned under the same conditions as before, except for the unavoidable variations in pressure and humidity of the surrounding air. Intercomparisons of these sources were made at the station and are as follows:

TABLE I

LAMP N_1 IN HEFNER CANDLES

	K 59 No. 1	K 113 No. 2
From Candle	0.88	0.93
From N_1	.93	.93
From N_2	.98	.98
Mean	0.93	0.95

For some reason there was a change between the two electric lamps, but if we refer N_1 to the mean of the three, we find the net variation not more than 2 per cent. As this is negligible compared with other possible errors, we assume that the mean of the three lights has not varied since 1918, and we adopt 0.93 candles for the lamp N_1 which was compared with the corona.

The program during totality included a first exposure to the corona and sky background, then to the sky alone 8° from the sun, back to the corona, and so on, with a stop near the middle of totality to check the zero of the galvanometer. The tubes were operated by Dr. L. B. Ham, of the department of physics, New York University, and the counting of seconds was done by Mr. A. S. Bibbins, a graduate of Wesleyan, while Messrs. Kunz and Stebbins read the galvanometers. It was convenient, as before, to take readings every 10 seconds, the photometer tubes being moved to the new position at each count of ten and then left undisturbed. A metronome was used, beating seconds. The start at totality was intentionally delayed for several seconds; Mr. Stebbins watched the disappearing crescent of the sun with a dark glass, and when sure of totality gave the signals at about 1-second intervals: "One-two-open." It was found much more satisfactory to begin in this leisurely way than by the abrupt signal "Go," and thus in some measure to relieve the

tenseness which unavoidably exists with the oncoming of totality. With the lag of the galvanometers, the best we could do was to get a measure of the corona at ten seconds after the beginning, and with the delayed start it is estimated that the first measure refers to the corona at about 10 seconds after second contact.

With other observers we went through the anxiety caused by the coming up of clouds at dawn of eclipse day, after a night, a whole day, and another night of clear cold weather. As we were gambling on the chance of a perfectly clear sky, it appeared that we were to get about what might have been expected. Fortunately for all concerned, the clearing of the sky about a half-hour before totality made all observations possible, and our own program went through without a hitch. At the uncapping of the tubes, the galvanometers were seen to move, and to move exactly as had been hoped for, and we could concentrate on getting the deflections as planned.

Both photo-electric cells were calibrated about an hour preceding totality, and then at about the same time after the eclipse. Each calibration curve showed a nearly linear relation between the intensity, computed by the law of inverse squares, and the galvanometer deflection.

Table II gives the readings and results during totality, which was predicted to begin at $14^h\ 12^m\ 30^s$, Greenwich civil time. In the first column the times are in seconds beginning with second contact, totality lasting 112 seconds. The second column is self-explanatory. The readings in the third column are as recorded at the time. The deflection in the fourth column was derived from an interpolated position of the zero. The values in Hefner candle meters in the fifth and sixth columns were derived from the calibration, while the values for the corona in the last column are rounded off to two decimals.

It will be seen that both observers agree in making the corona a trifle brighter at the first reading, and possibly a similar effect is present at the end. This could be due to the very bright inner corona which would be covered during the middle of totality. The measures of both corona and sky with the separate cells by the two observers are so nearly the same that it is sufficient to adopt the same mean for both, namely, 0.29 candle meters for the corona, and 0.12 candle meters for the area of sky observed.

We now come to the correction for atmospheric extinction which is the most unsatisfactory part of this work. This difficulty was realized in advance, and it was determined to make the best estimate

TABLE II

OBSERVATIONS DURING TOTALITY

SECONDS	EXPOSURE TO	GALVANOMETER READING	DEFLECTION	IN HEFNER CANDLE METERS		
				Corona+Sky	Sky	Corona Alone
	K 59 No. 1					
5	Dark	187	0.0			
15	Corona+sky	239	52.2	0.422	0.127	0.30
25	Sky	201.7	15.0			
35	Corona+sky	237	50.5	0.410	0.125	0.28
45	Sky	200.8	14.5			
55	Corona+sky	237.0	50.8	0.412	0.121	0.29
65	Dark	186.0	0.0			
75	Corona+sky	236.5	50.5	0.410	0.116	0.29
85	Sky	199.5	13.5			
95	Corona+sky	237.0	51.0	0.414	0.116	0.30
105	Sky	200	14.0			
115	Dark	186.0	0.0			
Mean					0.12	0.29
	K 113 No. 2					
5	Dark	251	0.0			
15	Corona+sky	278	27.0	0.422	0.116	0.31
25	Sky	258	7.0			
35	Corona+sky	276	25.0	0.391	0.116	0.28
45	Sky	258	7.0			
55	Corona+sky	276	25.0	0.391	0.115	0.28
65	Dark	251	0.0			
75	Corona+sky	276	24.8	0.390	0.112	0.28
85	Sky	258	6.6			
95	Corona+sky	277	25.4	0.397	0.115	0.28
105	Sky	259	7.2			
115	Dark	252	0.0			
Mean					0.11	0.29

possible of the extinction factor at the time, and then to stick to this no matter how the results came out. We could not take measures of the sun at various altitudes on eclipse day, as it was cloudy until the sun was well obscured by the moon, and then again before the moon passed off. The estimate was to be on the basis of 0.20

magnitude times the air-mass, times a factor based upon our judgment of the sky. In 1918 the factor adopted had been 1.8, while in 1925 the factor 2.0 was adopted. It might seem that this change of 10 per cent would scarcely cover the difference between the Wyoming sky from altitude 6500 feet and the Connecticut sky from altitude about 200 feet. Nevertheless, this was our deliberate judgment at the time. The stars during the night preceding were fully as bright as they are often seen from mountain stations, and from the blue color of the sky it was estimated that the transparency was almost as good as we had had in the desert air.

There is the further correction to mean distance of the earth from the sun, which in all strictness should be applied to make the

TABLE III

Date	1918	1925
Observed corona in candle meters	0.60	0.29
Zenith distance	53°.3	72°.3
Air-mass	1.67	3.26
Extinction at zenith in magnitude	0.36	0.40
Correction in magnitude	0.601	1.304
Log. reduction to no atmosphere	0.240	0.522
Log. reduction to mean distance	0.013	9.986
Log. observed corona	9.778	9.462
Sum	0.031	9.970
Corrected corona in candle meters	1.07	0.93

two results comparable. There is also a slight difference due to the different relative size of the moon's disk and its covering of the inner corona, which will be discussed later. The times of totality, however, were about the same—95 seconds in 1918, and 112 seconds in 1925. We have, then, the corrected results on two dates as in Table III. The air-mass is taken from A. Bemporad's table,[1] and is very nearly equal to the secant of the zenith distance.

As the corrected results come out, the corona of 1925 was some 13 per cent fainter than the one of 1918, but this difference is not enough to be considered as real. We can look at the problem in the other way, and working backward find what extinction factor in 1925 would be necessary to give equality for the corona on the different dates. This is readily found to be 2.2, corresponding to an ex-

[1] *Mitteilungen der Grossh. Sternwarte zu Heidelberg*, 4, 66, 1904.

tinction of 0.45 magnitude at the zenith, which is not very different from that assumed, and which might be considered possible. We had expected that if any such change as 25 per cent or 50 per cent were involved it could be detected, but to establish a variation of 10 or 15 per cent is better than can be done from these measures.

The eclipse of 1918 was at something less than a year following sun-spot maximum,[1] while the one of 1925 was probably at about the same interval after the succeeding minimum, which is not yet well determined. The two dates represent nearly the extremes of solar activity.

The question may be asked whether the prominences which were very bright in 1918 might not affect the results. The late Professor J. A. Parkhurst made a photometric study of the Yerkes direct photographs of 1918, and while his results were avowedly rough, they gave direct evidence on the question. He estimated that the total light of the prominences at that time was of the order of 2 per cent of the total light of the corona. This measure refers to the integrated effect on the photographic plate, and we have given in our earlier paper reasons for thinking that the prominences are of still less relative strength when measured with a photo-electric cell.

In 1918 the ratio of the reduced coronal light to that of the full moon was derived to be 0.50. The measures of the moon were not repeated in 1925 as it is felt that little further improvement could be made. With the same cells and light-sources, the full moon was measured in July, 1923, to be 2.18 Hefner candle meters as against 2.13 of the same units in 1918, which is near enough to call it the same.

We can now make a comparison with the results of G. H. Briggs at the eclipse of September 21, 1922.[2] He took similar measures with photo-electric cells and derived the light of the corona in terms of Hefner candle meters and of the full moon. There was a slight difference between the color-sensitivities of his two cells, and hence between the corresponding results for the corona; and he got a large variation during totality, which he ascribes to the moon gradually creeping over the inner corona on the eastern edge of the sun, and then later

[1] S. B. Nicholson, *Publications Astronomical Society of the Pacific*, **31**, 225, 1919.

[2] *Astrophysical Journal*, **60**, 273, 1924.

revealing a similar region on the west. His correction for extinction for zenith distance 69° was likewise very large. Taking the mean of his values at the middle of totality, we have 0.22 and 0.62 candle meters, respectively, for the observed and corrected values of the corona, the latter being 0.58 of our total light in 1918. If it is proper to neglect the prominences and chromosphere entirely, then these figures may be compared with our own on the basis of some assumed law for variation of the corona with distance from the limb or the center of the sun. This can, no doubt, be done on the photographs, but lacking this data at the present time we may make a rough estimate on the basis of some of the laws which have been proposed in the past.

Of the various empirical formulae derived for the light of the corona we may quote those of L. Becker[1] and Ö. Bergstrand.[2] Let J be the surface brightness of the corona at distance r from the center of the sun. Then the respective laws take the following form:

$$\begin{aligned} &\text{Becker,} \quad J=A_1/(r-0.720)^4 \\ &\text{Bergstrand,} \quad J=A_2/(r-1)^2 \end{aligned} \tag{1}$$

It was found by C. G. Abbot[3] in 1908 that Becker's law gave a very good representation for the total radiation of a corona at sun-spot maximum. For the corona of 1914, however, the elaborate study of Bergstrand showed that one simple law did not represent the mean light of the equatorial and polar regions, a fact which should be obvious on any photograph. We have given above his simplified expression for the equatorial region, though of course this must give too great a value for the corona's light at the very edge of the sun.

It is convenient to integrate the total light of the corona on the basis of each of these laws, and we have, respectively:

$$\left.\begin{aligned} L_1&=2\pi A_1\int_{r_1}^{r_2}\frac{r\,dr}{(r-0.720)^4}=-C_1\left[\left(\frac{r}{2}-\frac{0.720}{6}\right)\left(\frac{1}{r-0.720}\right)^3\right]_{r_1}^{r_2} \\ L_2&=2\pi A_2\int_{r_1}^{r_2}\frac{r\,dr}{(r-1)^2}=-C_2\left[\frac{1}{r-1}-\log\,(r-1)\right]_{r_1}^{r_2} \end{aligned}\right\} \tag{2}$$

[1] *Memoirs of the Royal Astronomical Society*, **57**, Appendix, p. 70, 1907.

[2] *Etudes sur la Distribution de la Lumière dans la Couronne Solaire* (Stockholm, 1919), p. 33.

[3] *The Sun*, p. 133.

The lower limit r_1 of the integrations is taken as the moon's semi-diameter, the sun's semi-diameter being unity, and the upper limit as $r_2=4$, corresponding to 2° radius of the field of our instrument, though in the first law $r_2=\infty$ is near enough.

In Table IV are the necessary data from the *American Ephemeris* and the calculated total light of the coronas at the three eclipses. If P_0 is the moon's horizontal parallax, for a given observer the moon's semi-diameter is to be increased by the factor $1+P_0 \cos z$, to reduce from the center of the earth to the station. The reduction to mean distance of the earth from the sun is neglected in this table.

TABLE IV

	1918, June 8 Rock Springs	1922, Sept. 20 Goondiwindi	1925, Jan. 24 Middletown
Sun's zenith distance	53°.3	69°	72°.3
Sun's semi-diameter	15′45″.3	15′56″.0	16′14″.7
Moon's semi-diameter	15 58.2	16 43.0	16 35.4
Moon's horizontal parallax	58 39	61 24	60 56
Ratio of apparent diameters, moon/sun $=r_1$	1.024	1.056	1.027
Computed relative light of corona (Becker)	1.00	0.77	0.98
Computed relative light of corona (Bergstrand)	1.00	0.47	0.90
Observed relative light of corona	1.00	0.58	0.88

Comparing the values for 1918 and 1925, it is seen that according to the two laws the 1925 corona would have been 2 per cent or 10 per cent fainter than in 1918. Therefore, assuming that the correction for atmospheric extinction is all right, it follows that the simplified Bergstrand law would account for all of the variation between the dates. Likewise, the comparison for Goondiwindi shows an observed result about midway between the computed values from Becker and Bergstrand. All of this discussion is perhaps beside the point before we have comparable photographic studies of the distribution of the coronal light at the three eclipses. The one conclusion which can be drawn, even now, however, is that there was no change in the total light of the corona between 1918 and 1925. The measured values at these dates agree within less than, say, 10 per cent.

We now consider measures of the brightness of the sky taken during and after totality. The adopted value for a circle 4° in diameter during totality is 0.12 candle meters. Shortly before fourth con-

tact, or at $15^h\ 07^m$ and $15^h\ 03^m$ Greenwich civil time, with cells 1 and 2, respectively, the sky was measured through apertures 2.44 and 2.50 mm. These gave 0.41 and 0.43 candle meters for the equivalent light. The two cells giving nearly the same, we adopt the results for Number 1 and reduce as we did in 1918 to an area about the size of the sun. For comparison, the results for 1918 are given, revised with an accurate calibration.

TABLE V

	1918	1925
Sky circle ½° diameter 8° from uneclipsed sun, in candle meters	5.7	10.4
Same during totality	0.0011	0.0019
Ratio	5300	5500

The sky at Middletown therefore measured about twice as bright as at Rock Springs, and the relative decrease due to the eclipse was very nearly the same. With the corona apparently half as bright as before, and the sky of double the brightness, the contrast between corona and sky was much less in 1925 than in 1918. Visual observers agreed that this last was a "light" eclipse, the brightness of the sky being due presumably to the general covering of snow over all the eastern states.

There has been some misunderstanding concerning the agreement of our measures in 1918, of the relative lights of the corona, moon, and sky, with the bolometric results of Abbot in 1908.[1] As Abbot's measures of the coronal intensity are in good accord with Becker's law,[2] we may use this law in deriving the ratio of the total lights of the corona and full moon from Abbot's published results for the surface intensity.[3] Let J_1 and J_2 be the measured surface brightnesses of the corona and moon, respectively, and in apparent angular measure let

r = distance from sun's center (sun's semi-diameter = 1)

r_0 = semi-diameter of moon at mean distance = 0.932

r_1 = semi-diameter of moon at time of eclipse = 1.043

r_2 = approximate outer limit of corona = 1.78

[1] S. A. Mitchell, *Eclipses of the Sun*, p. 346.

[2] *The Sun*, p. 133.

[3] *Lick Observatory Bulletin*, **5**, 19, 1908.

Abbot found the corona to be of intensity 13 at 1′.5 from the moon's limb, and from this we put $J_1 = 13$ and $r = 1.135$ in Becker's formula, $J_1 = A_1/(r-0.720)^4$, and derive $A_1 = 0.386$. Abbot observed the moon near last quarter and found its intensity to be 12 in arbitrary units, but we assume that the full moon would be four or five times as bright, and adopt 50 of his units for the approximate surface intensity.

Integrating as in (2) and substituting the numerical values, we obtain

$$\frac{\text{Corona}}{\text{Moon}} = \frac{2\pi A_1 \int_{r_1}^{r_2} \frac{r\,dr}{(r-0.720)^4}}{\pi J_2 r_0^2} = 0.2 \pm ,$$

which is of the same order as the value 0.5 determined with our photo-electric cell.

Similarly, for the moon and sky comparison of surface brightness we have

$$\text{Abbot (Flint Island)}, \quad \frac{\text{Moon}}{\text{Sky } 20^\circ \text{ from sun}} = \frac{50}{140} = \frac{1}{3} \pm$$

$$\text{Photo-electric (Rock Springs and Urbana)}, \quad \frac{\text{Moon}}{\text{Sky } 8^\circ \text{ from sun}} = \frac{2.1}{5.7} = \frac{1}{3} \pm$$

Abbot's value for the moon should be further increased because of atmospheric extinction, but his sky value at 20° distance should also be made larger to bring it up to the brightness at 8°. We therefore find no serious disagreement between the total-radiation results of the bolometer and the selective-radiation results of the photo-electric cell.

SUMMARY

We now bring together the principal results for the two eclipses.

The results show good agreement with the bolometric measures of Abbot in 1908, and with the photo-electric measures of Briggs in 1922.

Finally, the evidence all points toward little, if any, change in the total light of the corona between maximum and minimum of sun-spots.

TABLE VI

	1918	1925
Observed total light of corona	0.60 candle meters	0.29 candle meters
Same corrected to no atmosphere	1.07 candle meters	0.93 candle meters
Sky circle ½° diameter 8° from uneclipsed sun	5.7 candle meters	10.4 candle meters
Same during totality	0.0011 candle meters	0.0019 candle meters
Ratio of daylight sky to eclipsed sky	5300	5500
Observed ratio of corona to ½° circle of daylight sky	0.105	0.028
Corrected ratio of corona to full moon	0.50	.....

We cannot repeat too often an acknowledgment of our indebtedness to Professor Slocum and the members of his staff for the cordial reception and assistance we received at the Van Vleck Observatory. Also we thank Professor W. G. Cady for loan of apparatus from the Physics Laboratory at Wesleyan, and Professor R. H. Baker for the use of equipment from the University of Illinois Observatory.

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MEASURES OF THE RADIATION OF THE SOLAR CORONA OF JANUARY 24, 1925

By H. T. STETSON and W. W. COBLENTZ

ABSTRACT

Apparatus.—Observations of radiation of the solar corona were made at Middletown, Connecticut, during the eclipse of January 24, 1925, by means of a reflecting telescope, vacuum thermopile of special design with fluorite window, a D'Arsonval galvanometer, and a glycerin cell for obtaining approximate water-cell transmission of the radiation.

Results.—The mean of three series of measures indicated from 30 to 37 per cent radiation transmitted by a 1-cm cell of glycerin. The transmission of the glycerin was found to be practically identical with that of water under the same conditions. Proportionally more infra-red radiation from the corona than from the sun is indicated, in general accord with Abbot's results in 1908. A temperature of 3000° C. for the corona is tentatively suggested.

Conclusions.—The excess of infra-red now found is explained as due to difference in the screens employed. Cosmic dust and oxides of metals ejected from the sun are suggested as causes of this infra-red radiation. The supporting work of Nichols and Howes on luminescence of oxides is discussed.

The problem of the nature of the radiation of the corona has long been a puzzling one to astronomers. Estimates of the total amount of illumination have been made, varying from a small fraction to more than the equivalent of the light of the full moon. The conflicting testimonies have doubtless been due to the different methods employed as well as to probable differences in the intensity of the corona at different eclipses.

The work in 1908[1] of Abbot, using a bolometer, showed the intensity of the radiation from the corona at a distance of 1°.5 from the sun's limb to be about equal to that of full moon, while Stebbins' measures with the photo-electric cell in 1918 indicated that the total light of the corona was about one-half that of the light of the full moon.

After considering the work of previous observers, it seemed especially desirable that advantage should be taken of the eclipse of January 24, 1925, to attempt some measures of radiation which so far as possible would be capable of some interpretation independent of brightness of the adjacent sky, and free from selectivity on the part of the receiver.

[1] *Annals of Astrophysical Observatory of Smithsonian Institution*, 3.

The non-selective character of the thermopile, therefore, as distinguished from the more sensitive photo-electric cell, led to its adoption in the plans of the present investigation. From such material as was available, a Newtonian reflecting telescope of 15 cm (6 in.) aperture and 127 cm (50 in.) focal length was utilized. The mirrors were freshly silvered, and in order to make use of all available radiation, a fluorite window was used for the chamber in which the

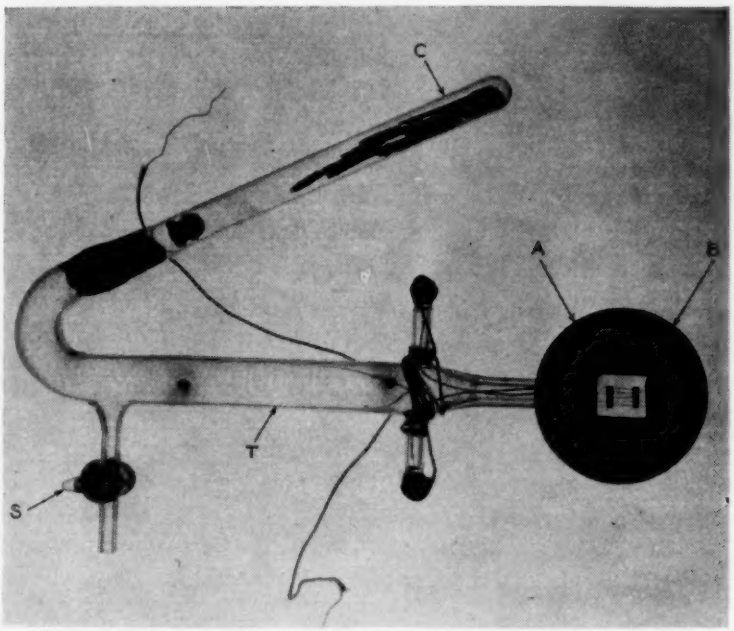

FIG. 1.—Vacuum thermopile for coronal radiation

vacuum thermopile was housed, thus assuring the transmission of as much of the infra-red radiation as possible.

In order that the thermal gradient between the hot and cold junctions of the thermopile should be standardized, they were arranged as in Figure 1, forming a symmetrical design, and of such dimensions as to be capable of being set simultaneously upon the dark disk of the moon during the moments of totality. In this way zero settings could be made with all junctions under the same condition and receiving practically zero radiation. Repeated tests by

Coblentz and Lampland at the Lowell Observatory, Flagstaff, Arizona, have shown zero radiation from the dark of the moon.

The thermopile itself consisted of five junctions of bismuth-silver wire, the bismuth being 0.085 mm in diameter, pressed flat, and the silver, 0.030 mm in diameter. The size of each receiving surface was 1.5 mm × 5 mm. The hot and cold receivers were identical in design and dimensions. Radiometrically they were balanced to within 3 per cent. That is to say, when both receivers were exposed to a standard of radiation or to the sky, a slight galvanometer deflection ensued, which was less than 3 per cent of the total deflection obtained when either receiver was exposed to radiation. The total resistance of the thermopile was 9 ohms.

By means of a slide carrier ingeniously constructed by Mr. D. W. Mann, mechanician at the Jefferson Physical Laboratory, the thermocouple could be quickly moved across the moon's disk so that either of the two receiving surfaces could be exposed to the radiation of the corona. The carrier for this thermopile cell was so designed that the whole affair could be quickly oriented about the eye-tube of the telescope without disturbing the focus, and securely clamped in any desired position.

The receiving surfaces of the thermopile could be brought into the focal plane of the mirrors by means of a rack and pinion. Just inside the focal plane of the telescope and in front of the receivers, a slide carrier was constructed to facilitate the interposition of a water cell, to obtain the transmission of energy through water as compared with the free readings through air. For reasons which will be explained later on, glycerin was used instead of water. Their transmission curves are practically identical.[1] The importance of determining the transmission of the radiation from the corona through the water cell can hardly be overemphasized, if data are to be obtained as to the character of the radiation of the corona.

If the light of the corona is largely high-temperature emission, then presumably the transmission of the water cell should be high, characteristic of a large percentage of radiation in the visible region of the spectrum; whereas, if a considerable amount of the radiation is in the infra-red, due to radiation at lower temperature, the amount

[1] *Bureau of Standards Scientific Papers* (No. 418), **17**, 272, 1921.

of radiation transmitted by the water cell should be relatively small. Therefore, results obtained in this way should have an important bearing upon any theories of the corona.

The site chosen for conducting this investigation was at Middletown, Connecticut, on the brow of the hill a short distance to the southeast of the Van Vleck Observatory. A most convenient and satisfactory shelter for all the apparatus (Fig. 2) was found in a

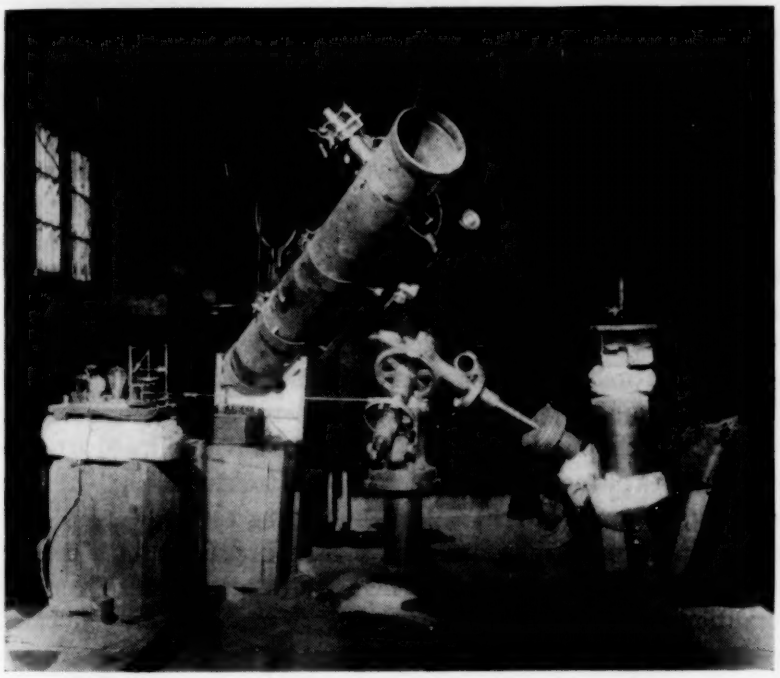

FIG. 2

concrete garage which was very generously placed at our disposal by Dr. Fauver, professor of physical education at Wesleyan University. Electric current for the driving-clock for the telescope and for reading lights was made available by the prompt action of Wesleyan University in supplying the necessary circuits a few days prior to the eclipse. The electrical driving-clock, loaned by the Whitin Observatory of Wellesley College, was actuated by a small motor of one-twentieth horse-power and ran with perfect satisfaction inde-

pendent of temperature or load. For a galvanometer pier a piece of drain pipe filled with sand and surmounted with stones and cement proved sufficiently rigid.

As many reports will detail weather conditions and other features connected with the eclipse, we need only say that for thirty-six hours prior to the event the weather was clear and cold, with temperatures around zero Fahrenheit and below, augmenting very considerably the usual difficulties under which adjustment of the apparatus could be made.

Upon final evacuation of the thermopile chamber on the morning of the eclipse, all joints were resealed with Kotinsky and shellac and gave promise of no difficulty through leakage. A very convenient and inexpensive arrangement for testing the degree of vacuum was improvised by the combination of one dry cell and a single unit Ford coil, which gave a satisfactory discharge between the sealed terminals contained in the auxiliary tube of the thermopile cell.

On the morning of the eclipse, January 24, 1925, clouds threatened, and the sun was more or less obscured during the partial phase but broke entirely clear a few minutes before totality ($9^h\ 12^m$ E.S.T.). The low altitude (17°) of the sun at Middletown had caused no little hesitation at the outset of our plans as to the advisability of attempting measures of radiation and of water-cell transmission. The clear, cold sky, however, of that Saturday morning assured less moisture in the atmosphere than could have been hoped for in a summer eclipse with the sun at a much higher altitude. Under the actual conditions of observation, the low altitude made it more convenient to operate the instrument, mounted entirely within the shelter of the garage, with exposure through its wide doors opening to the southeast.

As thermal difficulties and stray currents affected somewhat the stability of the galvanometer, it was impossible to prearrange an inflexible schedule for taking readings during totality. The galvanometer used in the final set-up was a D'Arsonval type, Model 89, manufactured by the Weston Electrical Instrument Company, and had a sensitivity of 12 mm per microvolt.

As no accurate prognostication of the throw of the galvanometer could be made and it would appear inadvisable to change the circuit

during totality, it was deemed safer to interpose sufficient resistance to prevent any possibility of the galvanometer deflections exceeding the reading limits of the scale. After preliminary trial, it was decided to operate with 40 ohms external resistance connected into circuit with the thermocouple. From trial settings made previous to totality, it was found that the galvanometer came to rest about 10 seconds after exposure of the thermocouple, and it was therefore decided that readings should thereafter be made after a lapse of 10 seconds from any given setting of the thermocouple, and this was done throughout the eclipse, seconds being counted from a stopwatch by Mrs. Coblentz.

The two receiving surfaces of the thermopile were designated *A* and *B*, receiver *A* being the one nearest the outlet tube of the cell. This tube is designated *T* in the figure and leads to the stopcock *S* and the calcium chamber *C* used for maintaining vacuum.

In making the readings, the cell was so placed that the receiving surfaces themselves extended north and south, the receiver *A* being always west of *B* as seen in the field of the telescope.

The program for taking readings was as follows:

Series I. No glycerin cell
- *a*) *A* and *B* both on dark of moon for zero reading
- *b*) *A* on the corona, 2′ west of sun's preceding limb
- *c*) *A* and *B* both on moon

Series II. Same as above with glycerin cell interposed

Series III. No glycerin cell
- *a*) *A* and *B* both on dark of moon for zero reading
- *b*) *B* on the corona, 2′ east of sun's following limb
- *c*) *A* and *B* both on moon

Series IV. Same as Series III with glycerin cell interposed

The frequent repeated readings on the dark of the moon gave opportunity to allow for any drift of the galvanometer zero that might occur, and the repetition of each series with the glycerin cell gave the data for determining the percentage of water-cell transmission of coronal radiation. The last reading of the fourth series was interrupted by the breaking out of the crescent sun and therefore had to be discarded. The settings of the thermopile receiver were made on the inner corona close to the dark limb.

The summary of the other series is as follows:

Series I.	No glycerin cell—corona west of sun	
	(1) Mean of zero readings *a* and *c*.....	11.3 cm
	(2) Reading with *A* on corona *C*.....	13.0
	Difference (2)−(1)	+ 1.7
Series II.	With glycerin cell—corona west of sun	
	(1) Mean of zero readings.....	10.6
	(2) Reading with *A* on corona.....	11.0
	Difference (2)−(1)	+ 0.4
Series III.	No glycerin cell—corona east of sun	
	(1) Mean of zero readings.....	8.8
	(2) Reading with *B* on corona.....	7.8
	Difference (2)−(1)	− 1.0

It will be noticed that the sign of the deflection in Series III is reversed, as it should be, since *B*, the cold receiver in Series I, was the warm receiver in Series III, and vice versa for receiver *A*.

If we take the mean of Series I and III, we have 13 mm for the mean deflection without the glycerin cell. Comparing this with the deflection of 4 mm in Series II, we get 31 per cent for the glycerin-cell transmission, or, corrected for reflection from cell and absorption by the two mirrors, 37 per cent. If we compare the glycerin-cell reading which was for the corona off the west limb of the sun with the corresponding reading for corona west of sun without glycerin cell, we get for glycerin-cell transmission the still lower value of 24 per cent, or corrected 30 per cent. Therefore, it appears from these results that we shall not be far wrong in stating that the glycerin-cell transmission of the inner-coronal radiation of the 1925 eclipse is of the order of 33 per cent with an uncertainty of perhaps 10 per cent.

In attempting to deduce the significance of this surprisingly low transmission of the glycerin cell, we seem to be forced to concede a large amount of infra-red radiation, unless some other factors, unknown and now unsuspected, have entered into the observations.

Before discussing further the interpretation of the low water-cell transmission, it should here be stated that while rehearsing operations on the day previous to the eclipse, the water cell froze solid in less than 10 minutes' exposure to the open. Therefore, on account of the cold weather at Middletown on the morning of the eclipse, and the attendant and almost certain danger of the water cell freezing

during the observations, glycerin was substituted for water in the cell, which necessitated the investigation of the transmission curve of glycerin. For this purpose, a liberal specimen of the actual glycerin used at the eclipse was preserved and its transmission determined by Coblentz. The transmission of a 1-cm cell of glycerin (also the sample used during the eclipse) was compared with a similar cell of water, with the same air temperature and the sun at the same altitude as during the eclipse. In both cases a transmission of 69 per cent was obtained, which is in agreement with previous measurements on water.

It is evident, therefore that the substitution of glycerin for water does not alter the conclusion which would have been deduced, if we had used water instead of glycerin. Glycerin, such as obtained in commerce, has the advantage of undercooling and will not freeze or become cloudy at a temperature far below 0° C. Recent tests at the Bureau of Standards on this, as well as other samples, show that glycerin can be cooled to −70° C. for several hours without freezing. Glycerin has a tendency to creep over the surface of the container. If care is taken that the windows do not become soiled, there seems to be no reason why glycerin should not be used in place of water in planetary radiometry.

Accepting, then, the result at its face value, we may look to the composition of the corona for its interpretation. From the calculated water-cell transmission from a black body, and from comparison with the water-cell transmission of stars[1] whose energy distribution has been measured and temperatures calculated, it would appear that the black-body temperature of the corona should be around 3000° C. When it is remembered that the corona is seen in perspective and that, while the receiver of the thermopile was set near the moon's limb, a considerable depth of the coronal material extending long distances from the sun was simultaneously contributing its energy to the thermopile, it will be evident that a large percentage of coronal radiation must come from relatively low-temperature emission, otherwise the low value of glycerin-cell transmission would not have been obtained. We may therefore conjecture that, aside from whatever other sources of radiation may exist in the corona,

[1] *Bureau of Standards Sci. Paper* (No. 438) **17**, 741, 1922.

we may have to consider a large amount of cosmic dust or other particles in the neighborhood of the sun (or particles thrown out by the sun), which, illuminated by the sunlight, is a considerable factor in giving the appearance of the corona and causing the observed continuous spectrum crossed by the Fraunhofer lines. The well-known polarization of the light from the corona is direct and independent evidence of the existence of finely divided matter in the neighborhood of the sun. Such material particles continuously exposed to the intense heat of the sun will not only reflect some sunlight, but also absorb solar radiation and re-emit it with a large amount of energy in the infra-red. Such being the case, we should get the low water-cell transmission which the results of this investigation appear to show. It certainly would seem that, whatever the cause of the bright emission lines in the coronal spectrum, such emission should be but a comparatively small part of the total radiation of all wave-lengths sent to us through the region of space in the immediate neighborhood of the sun. It is probably wise to postpone further discussion of this point until spectroscopic results on the corona of 1925 have been published by those working in that field. If it shall be further substantiated that a considerable amount of such cosmic matter exists and is responsible for much of the coronal radiation observed, it may become an important question whether such a cosmic cloud is entirely circumsolar, but the discussion of this point had best be left to consideration elsewhere.

The recent work of E. L. Nichols and H. L. Howes,[1] on the luminescence of oxides shows that at temperatures of 1100°–1500° C., the oxides of beryllium, magnesium, calcium, silicon, and zirconium, show emission of blue-green light in the region of 4500 A to 5200 A of an intensity out of all proportion to black-body radiation. While these outbursts of luminescence do not necessarily require the presence of hydrogen and oxygen, the work of Nichols and Howes shows that the phenomenon is enhanced by these gases. This may well have an important bearing on the physics of the corona. At the relatively low temperature of the corona, we might well expect the existence of particles of oxides, of calcium, and of other elements, which, held in suspension by light-pressure and convection, and

[1] *Physical Review* (2), **19**, 300, 1922.

heated by the intense radiation from the photosphere, would re-emit much radiation in the infra-red; and yet, at the same time, according to the experiments of Nichols and Howes, give out a brilliant luminescent light, which would contribute to the characteristic color of the coronal light. Therefore, the low water-cell transmission, which we have observed, would not be inconsistent with the blue light emitted, but might very well be interpreted as evidence in support of the critical luminescent temperatures discovered by Nichols and Howes. This luminescence would account for the rapid falling off in intensity in the red end of the photographs of the spectrum of the corona.

In summarizing, we can perhaps do no better than to compare our results with the bolometric work of Abbot at the eclipse of 1908—the only previous data available where a black-body receiver was employed. It is to be noted that the window of the bolometer chamber then used was of glass 3 mm thick, so that the radiation examined was limited to wave-lengths shorter than 4 μ. In place of a water cell, Abbot made use of a glass screen 3 mm thick covered on one side with asphaltum varnish. Such a film of asphaltum absorbs all visible radiation and has a high and practically non-selective transmission for infra-red rays throughout the spectrum to the 4 μ limit of the glass backing.[1] Abbot's measurements on the corona at a distance of one-tenth and one-fourth the radius of the sun from the limb showed a screen transmission of 36 per cent, whereas for the sun proper a transmission of but 33 per cent of infra-red was obtained. This shows, therefore, 9 per cent more infra-red radiation from the corona than from the sun. We must remember, however, that, since the glass window limited the radiation observed to practically 4 μ, any infra-red radiation of greater wave-length would be unobserved. In comparing our results with those of Abbot, it is important to note that there is agreement in an indication of proportionally greater infra-red radiation from the corona than from the sun. The much larger value of infra-red radiation from the corona which we obtained might be well accounted for by the substitution of fluorite for the window of the receiver as compared with the glass

[1] Coblentz, "Supplementary Investigations of Infra-Red Spectra," *Publication* No. 97, Carnegie Institute of Washington.

used in the earlier work. The fluorite window would transmit infrared radiation (of wave-lengths 8 to 12 μ transmitted by the earth's atmosphere) which would be excluded by the glass window used by Abbot.

In conclusion, the authors wish to express their appreciation to Professor Frederick Slocum, director of the Van Vleck Observatory, for the facilities afforded us at Wesleyan; and particularly to Professor Edgar Fauver for so very kindly placing at our disposal the use of his garage for the entire week of the eclipse, at no little inconvenience to himself; to Professor W. K. Greene, of the Amherst College Observatory for the loan of the reflecting telescope; and to Professor John C. Duncan, of the Whitin Observatory of Wellesley College, for the loan of the driving clock. To the painstaking co-operation of the other members of the party, Mrs. Coblentz, Mrs. Stetson, Mr. D. W. Mann, and to Professor Albert S. Hill, of the chemistry department of Wesleyan, much credit is due for the success of the undertaking. Toward the expenses of the expedition we gratefully acknowledge the very liberal assistance of Mrs. Robert Wheeler Willson and Mr. R. Bruce Barbour.

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ORBIT OF THE SPECTROSCOPIC BINARY 16 LACERTAE

By OTTO STRUVE and N. T. BOBROVNIKOFF

ABSTRACT

The orbit of the spectroscopic binary 16 Lacertae was derived from thirty-one spectrograms obtained with the one-prism Bruce spectrograph of the Yerkes Observatory. The period is $12^d.3106$. The *Ca* lines H and K show a stationary velocity of -18.9 km/sec., while the velocity of the center of mass of the binary is -6.9 km/sec. The component of the solar motion in the direction of this star is $+10.3$ km/sec.

The binary character of this star was discovered in 1910 by Professor O. J. Lee[1] from measurements of three spectrograms obtained with the Bruce spectrograph. Twenty-eight additional spectrograms were secured during the winter of 1924–25. We are greatly indebted to Professor S. B. Barrett for part of the observations used in this paper. All the spectrograms measured for the determination of this orbit were obtained with the dispersion of one prism.

The position of 16 Lacertae (Boss 5913) for 1900 is $\alpha = 22^h51^m.9$, $\delta = +41°4'$. Its visual magnitude, as given in the *Henry Draper Catalogue*, is 5.54; and its photographic magnitude, according to the same source, is 5.37. Its spectral type is B3. The spectral lines in this star are numerous and fairly sharp, so that the precision of measurement is perhaps a little above the average for stars of this spectral class. The calcium lines H and K are sharp, and their stationary character was noted by Mr. Lee in his examination of the first three spectrograms. The velocities derived from these lines were not included in the averages used for the determination of the orbit. They are given separately in Table I. These calcium velocities did not show any relation to the velocity curve of the binary system, and it is safe to assume that they are stationary within the accuracy of measurement. The range in velocity of 28 km/sec. exhibited by the calcium lines seems unusually large, but this is probably attributable to instrumental errors. On our plates the calcium lines are rather far from the center, and differences in focus or in the

[1] *Astrophysical Journal*, **32**, 307, 1910.

strength with which the comparison spectrum is impressed on the plate are liable to produce much larger errors near the ends of the spectrum than in the center.

From ten to seventeen stellar lines were measured on each spectrogram. The wave-lengths used for the stellar lines as well as for the titanium and iron comparison lines were those which are regularly employed at the Yerkes Observatory. Although it is recognized that some of these wave-lengths are slightly in error, it seemed preferable to use the same set of wave-lengths which had been used in all previous computations in order to make the velocities determined for 16 Lacertae directly comparable with other velocities determined with the Bruce spectrograph. A full discussion will soon be made of all radial velocities of B-type stars determined at the Yerkes Observatory, and corrections to individual line velocities will at that time be introduced to compensate for differences between old and new laboratory wave-lengths.

A very interesting absorption line in the spectrum of 16 Lacertae was noticed at λ 4470.0 in the immediate vicinity of the helium line 4471.646. This faint line does not seem to belong to any of the chemical elements usually met with in stars of the Orion type. Only on the best spectrograms is it completely separated from the helium line. On plates of poorer definition the two lines are blended, and for this reason several velocities determined from the helium line were rejected. The accurate wave-length and some of the characteristic features of this line will be dealt with in a separate note.

The appearance of the lines on the first few plates of this star suggested that possibly the fainter component of the double was also impressed on the spectrograms. The close companion to the helium line also made us believe at first in the visibility of the fainter component of the binary. However, it was soon recognized that the faint line at 4470.0 could not be due to the second spectrum but belonged to the light of the principal star, as did the other spectral lines. A careful examination of the best plates leads us to the conclusion that only one component of the binary is visible on our spectrograms.

The period was determined from the observations of 1924–25 and later adjusted in order to represent the old observations of 1909. Unfortunately, there were no observations available during any of

the intervening years. Such observations would have greatly improved the period.

TABLE I*

Plate	G.M.T.	Observed By	Qual.	Vel. km/sec.	Vel. *Ca* Lines km/sec.	O.−C.
IB 2110.....	1909 Aug. 23.709	F, S	g	−32.7	−14.6	(− 5.5)
2178.....	Nov. 8.696	L, S	g	+ 6.2	−12.0	(+10.2)
2188.....	Nov. 22.597	L, S	p	+11.0	.....	(− 0.9)
IR 7497.....	1924 Sept. 22.633	σ, S	g	+21.5	−34.7	+ 5.3
7504.....	Sept. 24.794	B, σ, S	f	− 4.4	.....	− 2.4
7507.....	Sept. 26.568	σ, S	g	−22.3	.....	− 2.3
7509.....	Sept. 28.551	B, σ, S	f	−20.3	.....	+ 6.4
7512.....	Sept. 28.787	B, σ, S	g	−25.1	.....	+ 1.4
7513.....	Sept. 28.866	σ, S	g	−32.3	.....	+ 4.3
7515.....	Sept. 29.660	σ	p	−19.8	.....	+ 3.9
7516.....	Sept. 29.808	σ, B, S	f	−20.7	.....	+ 2.3
7518.....	Oct. 1.550	B, σ, S	g	−10.6	.....	− 1.7
7519.....	Oct. 1.725	B, S	f	− 4.0	.....	+ 3.0
7520.....	Oct. 1.823	B, σ, S	p	− 7.7	.....	+ 0.2
7523.....	Oct. 4.558	σ, S	g	+22.5	.....	+ 5.0
7524.....	Oct. 5.557	σ, S	f	+ 8.4	.....	− 5.7
7526.....	Oct. 5.765	σ, S	g	+ 6.0	.....	− 6.6
7529.....	Oct. 7.715	σ, S	f	− 5.5	.....	+ 3.2
7530.....	Oct. 8.729	σ, S	g	−17.7	.....	+ 1.2
7531.....	Oct. 16.583	σ, S	g	+17.2	−6 .5	+ 0.4
7533.....	Oct. 16.737	σ, S	p	+10.3	.....	− 7.0
7539.....	Oct. 19.547	σ, S	f	− 1.4	.....	+ 2.2
7548.....	Oct. 22.578	σ, S	g	−34.7	−25.3	− 8.4
7559.....	Oct. 25.540	σ, S	g	−20.7	−20.2	− 5.7
7565.....	Oct. 26.542	σ, S	g	− 4.8	−20.1	− 0.1
7571.....	Oct. 29.550	σ, S	f	+19.3	.....	+ 2.0
7636.....	Dec. 27.493	σ, S	f	− 3.9	.....	− 3.5
7646.....	1925 Jan. 5.984	σ, S	g	−24.1	−20.3	+ 0.4
7655.....	Jan. 8.018	B, S	g	− 8.7	−18.3	+ 0.4
7663.....	Jan. 10.993	σ, S	g	+ 9.5	−16.8	− 6.2
7668.....	Jan. 15.005	B, S	f	−13.6	.....	− 0.4

* In Table I the time of observation is given in Greenwich Civil Time for observations made after January 1, 1925. The names of the observers and the quality of the plates, are indicated as follows: B=S. B. Barrett, F=E. B. Frost; L=O. J. Lee; S=F. R. Sullivan; σ=O. Struve; f=fair; g=good; p=poor.

All of the spectrograms were measured by Struve, and in addition to this several plates were remeasured by Bobrovnikoff. The means of both measures were taken in such cases.

The observational material is collected in Table I. The values of O.−C. in the last column are those which resulted from the final determination of the orbit.

A preliminary graphical solution was made according to the method of Lehmann-Filhés, with a period of $12^{d}.3106$. A least-squares

solution was then carried out by Bobrovnikoff by means of the tables computed by Professor Schlesinger.[1] The preliminary and the final elements and their probable errors are given in Table II. The representation of the observations is only slightly improved in the second orbit: The value of $[pv^2]$ was reduced from 420 to 408. The probable error of one plate of good quality was found to be ± 2.8 km/sec., which can be considered as a good result for a star of this spectral type. Most of the values of O.−C. appear to be well within the limits of possible errors of measurement. In fact, some of the greatest differences occur between plates obtained at nearly the same phase or even between plates of the same night, e.g., No.

TABLE II

ELEMENTS

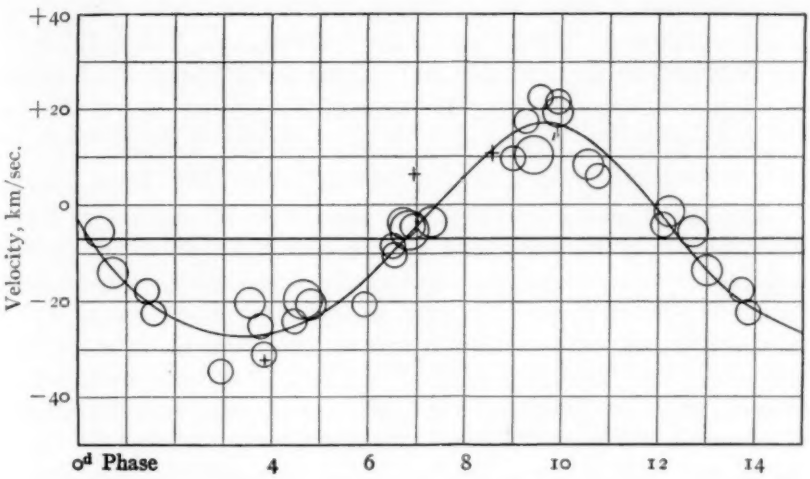
Preliminary	Final	Probable Errors
$\gamma = -7.5$ km/sec.	-6.9 km/sec.	.....
$P = 12^d.3106$	$12^d.3106$	.....
$e = 0.14$	0.10	± 0.03
$K = 22.2$ km/sec.	22.2 km/sec.	± 1.0 km/sec.
$\omega = 9°.8$	$7°.8$	$\pm 8°.5$
T = J.D. 2424063.900	2424063.894	$\pm 0^d.016$
$a \sin i$ =	3,650,000 km	.....

7531 and No. 7533, which give a difference of 7 km/sec. Therefore it did not seem necessary to attempt any further refinements.

The average velocity of the *Ca* lines H and K is -18.9 km/sec., with a probable error of ± 1.6 km/sec. The probable error of one determination of a calcium velocity is ± 5.2 km/sec. for each plate. The component of the solar motion in the direction of 16 Lacertae is $+10.3$ km/sec. The calcium which produces the stationary lines in the spectrum of this star is therefore not at rest with respect to the stellar system from which the solar motion had been derived. The final value adopted for the velocity of the center of mass of the binary is -6.5 km/sec. This value is closer to the component of the solar motion than is the velocity derived from the calcium lines. The star itself is therefore more nearly at rest with respect to the stellar system than is the calcium cloud. The residual velocity of

[1] *Publications of the Alleghany Observatory*, 1, 33, 1908.

8.9 km/sec. between the velocity of the sun and that shown by the calcium lines is decidedly too large to be explained by instrumental errors.



The velocity curve of this spectroscopic binary is shown in the figure. Phase $0^d.000$ corresponds here to J.D. 2424054.000. The individual observations of 1924–25 are represented by open circles, whose radii are taken equal to their respective probable errors. The crosses represent the observations of 1909. The letter *P* denotes the time of periastron passage.

YERKES OBSERVATORY
April 17, 1925

REVIEWS

Grundzüge der Theorie der optischen Instrumenten nach Abbe. Von SIEGFRIED CZAPSKI und OTTO EPPENSTEIN. Third Edition. Revised by the scientific staff of the Zeiss Works: H. BOEGEHOLD, O. EPPENSTEIN, H. ERFLE, A. KÖNIG, M. v. ROHR. Edited by H. ERFLE and H. BOEGEHOLD. Leipzig: Johann Ambrosius Barth, 1924. Pp. xx+747. Figs. 316. Price, $7.25.

During the twenty years that have passed since the appearance of the second edition of this well-known work on geometrical optics and optical instruments, many important advances have been made. In order that proper mention of these more recent researches might be included in the third edition, the authors found it necessary to revise much of the text and to practically re-write portions of the book. That the scientific papers of recent times have been carefully searched is evident from the multitude of references which have been collected according to author at the end of the volume. This, in connection with a good index, expedites reference to the original papers on any topic. At the same time it avoids the undesirable breaking of continuity sometimes caused by running numerous references in the body of a text.

In the first chapter, which is devoted to fundamental principles, the conceptions of Sturm regarding elementary pencils have been replaced by those of Gullstrand. The chapter on spherical aberration has been made into two, thus permitting fuller discussion of the contributions of Hamilton, Gullstrand, Schleiermacher, Libotzky, Stähle, and others. The recent work of T. Smith is briefly outlined. In a new short chapter, some of the very special optical instruments used in medicine are discussed briefly. In the chapters on the eye and on vision one finds new material, while the modern developments in instrument design have added considerably to the chapters devoted to the telescope, the microscope, and to other instruments. Whether one is looking for information on theory or on applications in instruments he will find mention of the more noteworthy contributions.

All who use optical apparatus in scientific work may find something of interest and value in the book. The old editions have long been favorites with students of practical optics. No doubt the new edition will prove to be even more helpful.

G. W. MOFFITT